ATOMIC COLLISION THEORY

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Preface

Although the theory of atomic collisions is fundamental to many branches of physics and astrophysics, hardly any text books are available at an introductory level, although at a more advanced level, the established research worker is well served by N. F. Mott and H. S. W. Massey's treatise on 'The Theory of Atomic Collisions' (Oxford, 3rd edit., 1965) which originally appeared in 1933 and which will remain the indispensable classic in the field. This book, which is based on my lectures delivered in the Spring of 1968 at the University of Washington, is intended to fill this gap in the literature. It is primarily addressed to graduate students, but in addition, it contains a survey of the most recent developments in the field that will be of interest to more senior physicists. The book is not addressed solely to intending theorists, but it is hoped it will be of equal value to experimentalists in assessing the theoretical interpretation of their investigations. It should be understood easily by all those who have attended a good undergraduate course in non-relativistic quantum mechanics.

The first four chapters provide a self-contained account of non-relativistic quantum scattering theory. In Chapter 1, the theory of scattering of particles by a central potential is developed and is followed in Chapter 2 by a discussion of a number of important practical methods for the approximate calculation of cross sections, including those based on variational principles and semi-classical approximations. The long range potentials between atoms decrease as some inverse power of the inter-atomic distance. Such potentials require special treatment and this topic forms the subject of Chapter 3. In Chapter 4, the theory is generalized to treat the collision of complex systems and the idea of the scattering or S-matrix is introduced.

In the second half of the book, the theory developed earlier is applied to a variety of problems in atomic physics. In each case the present state of the theory is outlined and the theoretical predictions

are compared with the latest experiments. Chapters 5 and 6 are concerned with the interactions of electrons with atoms, while Chapter 7 contains a detailed account of the auto-ionizing states that are responsible for the recently discovered resonances in the scattering of electrons at energies below the excitation thresholds of the target atoms. Chapters 8 and 9 review the theory of heavy particle collisions between atoms and ions and particular attention is paid to the theory of charge exchange. The application of scattering theory to the collisions of electrons with molecules is a complex problem, but recently some successes have been achieved and these are described in the last chapter.

Although no attempt has been made to provide a comprehensive bibliography, extensive references to the original papers are collected together at the end of each chapter and it is hoped that these will help to overcome the often considerable difficulties facing the new research worker in finding his way through the literature.

It is pleasant to thank Professor R. Geballe and his colleagues at the University of Washington for their hospitality during the period that the major part of this book was written, and for providing the ideal conditions for study and research, and my particular thanks are due to Jim Martin and Harold Zimmerman who gave me invaluable help in collating the manuscript of my lectures and in the preparation of many of the figures and diagrams, and to Dr. M. I. Barker for his careful reading of the proofs. I am indebted to the Editor of the 'Proceedings of the Royal Society' for permission to reproduce Figures 5-3 and 6-4. Finally, I should like to express my appreciation to Mrs. Dorothy Birtles for her expert typing of the final manuscript.

Durham, England   Brian H. Bransden
September 1969

Note On Units

With the exceptions noted below, atomic units are generally used throughout the text. In these units $h = m = e = 1$, where h is Planck's constant divided by (2π), m is the mass and e the charge of the electron. The atomic unit of energy is equal to 27.2 electron volts, the unit of length is the Bohr radius of the hydrogen atom $a_0 = 0.5292 \times 10^{-8}$ cm, while the unit of time is equal to 0.242×10^{-16} sec. Scattering cross sections have the dimensions of an area and the unit cross section is a_0^2 cm^2, that is 0.281×10^{-16} cm^2.

When quoting experimental data or the results of theoretical calculations, the units employed in the original papers are given. Most frequently energies are in electron volts and cross sections in cm^2. It is occasionally convenient to employ Angström units of length (1 A $= 10^{-8}$ cm), in which case the unit cross section is $1(A)^2 = 10^{-16}$ cm^2.

A Note from the Publisher

This volume was printed directly from a typescript prepared by the author, who takes full responsibility for its content and appearance. The Publisher has not performed his usual functions of reviewing, editing, typesetting, and proofreading the material prior to publication.

The Publisher fully endorses this informal and quick method of publishing lecture notes at a moderate price, and he wishes to thank the author for preparing the material for publication.

Contents

Chapter 1

POTENTIAL SCATTERING

The interactions between atoms, or between electrons and atoms, are studied through scattering experiments in which a well defined beam of particles is allowed to interact with the atoms of a target and the products of the collision are detected and measured. It is necessary to describe such an experiment in quantum mechanical terms and to achieve this several simplifying assumptions will be introduced, that are satisfied in most of the experiments in which we are interested. The target will be supposed to be so thin that the probability that any particle in the beam is scattered by more than one atom in the target can be neglected, and it will be assumed that the density of particles in the beam is so low that the beam particles do not interact with each other. We shall further suppose that each particle in the beam has the same definite value of energy and momentum. In view of this, the wave function of an incident particle is an eigenfunction of momentum and energy and, by the uncertainty principle, it is not localized in space or time. In the position representation, the wave function is the plane wave

$$\varphi(\mathbf{r},t) = \varphi_{\mathbf{k}}(\mathbf{r})e^{-iEt/\hbar}; \quad \varphi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{1-1}$$

As we shall deal exclusively with particles moving at non-relativistic velocities $v \ll c$ the relationship between the energy E and the momentum $\mathbf{p} = \hbar\mathbf{k}$ is:

1

$$E = \frac{P^2}{2m} = \frac{\hbar^2 k^2}{2m} \; ,$$

(1-2)

where m is the mass of the incident particle and $\hbar = \dfrac{h}{2\pi}$,
where h is Planck's constant.
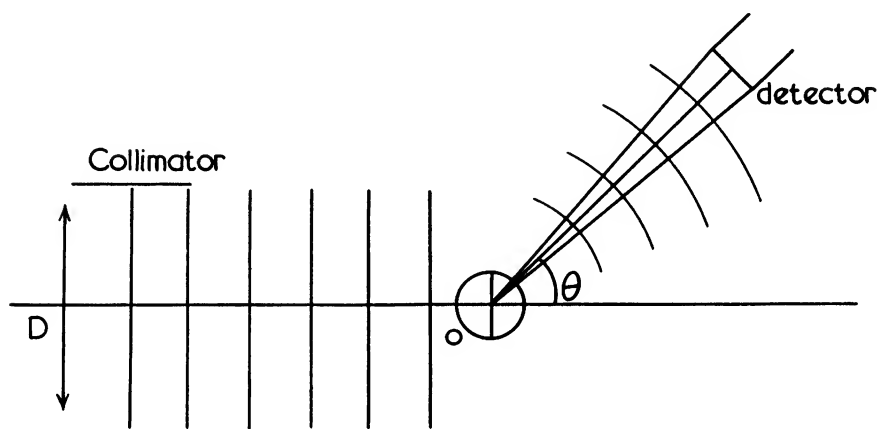
Figure 1-1.   Schematic diagram of scattering experiment.

In a real experiment, the incident beam is defined by
collimator slits, shown diagrammatically in figure 1-1, and is
therefore localized in space, but because the radial dimensions
of the beam are of the order 10^{-1} cm, while the dimensions of
an atom in the target are $\sim 10^{-8}$ cm, the uncertainty introduced
in the momentum can be neglected and the wave function can
be taken to be the plane wave (1-1). In the same way, the
beam is switched on for times that are long on the atomic time
scale. This allows us to treat the wave train as being of in-
finite duration in time and the uncertainty in energy of the
beam particles can be neglected. The results that we shall
obtain, based on these approximations, can be justified rigor-
ously by explicitly constructing a localized wave packet to
represent the incident particle and following its motion (Brenig
and Haag, 1959).

If the atoms of the target are very heavy compared with
the incident particles (which may be electrons for example),

they can be treated as fixed centers of force. The Schrödinger equation for the incident particle is then, in the position representation,

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right)\Psi(\mathbf{r},t) = i\hbar\frac{\partial\Psi(\mathbf{r},t)}{\partial t}, \tag{1-3}$$

where $V(\mathbf{r})$ is the effective potential field exerted by the target on the incident particles, and the position vector $\mathbf{r}$ of the scattered particle is measured from an origin situated at the fixed center of force.

In this chapter we shall consider potentials that are spherically symmetrical, $V(\mathbf{r}) = V(r)$, and of short range so that $V(r) \to 0$ as $r \to \infty$ faster than any inverse power of r. Examples of such potentials are the exponential well, $V(r) = A\exp(-r/a)$, the Yukawa well, $V(r) = r^{-1}A\exp(-r/a)$ and the spherical well, $V(r) = A$, $r < a$, $V(r) = 0$, $r > a$. The parameter A is known as the well depth and a is the range. For the moment it is assumed that V is real, $V = V^*$.

Under the steady state conditions that we have postulated, the system will be in an eigenstate of energy and we can write

$$\Psi(\mathbf{r},t) = \Psi(\mathbf{r})e^{-iEt/\hbar}, \tag{1-4}$$

where the time independent wave function $\Psi(\mathbf{r})$ satisfies

$$(\nabla^2 + k^2 - U(r))\Psi(\mathbf{r}) = 0, \tag{1-5}$$

and $U(r) = (2m/\hbar^2)V(r)$.

At large r, the particles scattered by the center of force will be represented by outgoing radial waves and if Ψ^A is the asymptotic form of $\Psi(\mathbf{r})$,

$$\Psi(\mathbf{r})_{r\to\infty} \sim \Psi^A(\mathbf{r}),$$

we have

$$\Psi^A(\mathbf{r}) = \varphi_{\mathbf{k}}(\mathbf{r}) + f_{\mathbf{k}}(\theta)e^{ikr}/r, \tag{1-6}$$

where (θ,φ) are the polar angles of $\mathbf{r}$, taking the incident direction $\hat{\mathbf{k}}$ as axis. The first term represents the incident plane wave and the second the radial outgoing wave. As the system is symmetrical about the direction of incidence, the scattering amplitude $f_{\mathbf{k}}(\theta)$ depends only on k and the angle of scattering θ. This is of course true only for spherically

symmetrical potentials and in general the scattering amplitude
is a function of both θ and φ.

1-1   THE CROSS SECTION

The wave function $\Psi(\mathbf{r})$ is not normalizable, but it can
be interpreted by identifying $\rho \equiv |\Psi(\mathbf{r})|^2$ with the particle
density in a beam of identical non-interacting particles. The
number of particles entering a certain closed volume V per
unit time is then given by

$$N = \frac{\partial}{\partial t} \int_V \rho dv = \int_V \left[\Psi^*(\mathbf{r},t) \frac{\partial}{\partial t} \Psi(\mathbf{r},t) + \Psi(\mathbf{r},t) \frac{\partial}{\partial t} \Psi^*(\mathbf{r},t) \right] dv. \tag{1-7}$$

Using the Schrödinger equations for Ψ and Ψ^* we have, provided
V is real,

$$N = \frac{i\hbar}{2m} \int_V (\Psi^*\nabla^2 \Psi - \Psi \nabla^2\Psi^*)dv. \tag{1-8}$$

This can be converted by Green's theorem to an integral over
the surface S that bounds the volume V, giving

$$N = \int_S \mathbf{j} \cdot \mathbf{n} \, ds, \tag{1-9}$$

where

$$\mathbf{j} = \frac{\hbar}{2mi} (\Psi^*\boldsymbol{\nabla} \Psi - \Psi\boldsymbol{\nabla}\Psi^*), \tag{1-10}$$

and $\mathbf{n}$ is a unit vector in the direction of the outward drawn
normal to the surface. The vector $\mathbf{j}$ is equal to the number of
particles crossing unit area of the boundary surface per unit
time in the direction of $\mathbf{n}$, it is called the current density
vector and satisfies (from 1.7 and 1.8) the conservation law,

$$\frac{\partial \rho}{\partial t} + \boldsymbol{\nabla} \cdot \mathbf{j} = 0. \tag{1-11}$$

The incident flux F is defined as the number of particles per
second in the incident beam crossing unit cross sectional area
normal to the beam, and F can be calculated by inserting the
plane wave $\varphi_{\mathbf{k}}(\mathbf{r})$ given by (1-1) into (1-10),

$$F = |\mathbf{j}| = \frac{\hbar k}{m}. \tag{1-12}$$

The outgoing radial current j_r can be found in a similar way from the second term in (1-6). For large r, neglecting terms of order $1/r^3$, we have

$$j_r = \frac{\hbar}{2mi} \left(\Psi^* \frac{\partial \Psi}{\partial r} - \Psi \frac{\partial \Psi^*}{\partial r} \right) \xrightarrow[r \to \infty]{} \frac{\hbar k}{mr^2} |f_k(\theta)|^2. \qquad (1-13)$$

From the radial current, we can calculate the number of particles, W, entering a detector per unit time. If the detector subtends a solid angle $d\Omega$ at the scattering center in a direction (θ, φ), then

$$W = j_r r^2 \, d\Omega(\theta, \varphi) = \frac{\hbar k}{m} |f_k(\theta)|^2 \, d\Omega(\theta, \varphi). \qquad (1-14)$$

The results of an experiment are usually expressed in terms of a differential cross section $(d\sigma/d\Omega)$ that is defined as the number of particles scattered in direction (θ, φ) per unit solid angle per unit incident flux:

$$\frac{d\sigma(\theta)}{d\Omega} = |f_k(\theta)|^2. \qquad (1-15)$$

To obtain a measure of the scattering without regard to angle, the total cross section σ is defined by integrating $d\sigma/d\Omega$ over all solid angles,

$$\sigma = \int_{4\pi} \left(\frac{d\sigma}{d\Omega} \right) d\Omega. \qquad (1-16)$$

In defining the cross section, the flux of the incident wave is calculated separately from that of the scattered wave. This procedure is justified provided that the detector is situated so that it lies well outside the incident beam as in figure 1-1 and collects only the scattered particles.

If only elastic scattering is possible, as many particles must enter any sphere drawn round the scattering centre as leave it, and the net radial flux calculated from both terms in (1-6) must vanish, but if inelastic scattering is possible particles will be absorbed from the incident beam and the net radial flux will no longer vanish. When the target can be excited, as in the case of electron scattering by atoms, inelastic scattering can take place giving rise to absorption from the incident beam. As far as the elastic scattering is concerned, the presence of such inelastic processes can be

incorporated phenomenologically by allowing the potential to become complex,

$$V = V_R + iV_I.$$

The Schrödinger equations for Ψ and $\Psi*$ are now

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V - i\hbar\frac{\partial}{\partial t}\right)\Psi(\mathbf{r}) = 0$$

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V* + i\hbar\frac{\partial}{\partial t}\right)\Psi*(\mathbf{r}) = 0. \tag{1-17}$$

The number of particles entering a volume V per second is

$$N = \frac{\partial}{\partial t}\int_V |\Psi|^2\,dv$$

$$= \frac{i\hbar}{2m}\int_V (\Psi*\nabla^2\Psi - \Psi\nabla^2\Psi*)\,dv + \frac{2}{\hbar}\int_V V_I|\Psi|^2\,dv. \tag{1-18}$$

The first term is, as before, $\int \mathbf{j}\cdot\mathbf{n}\,ds$, and gives the net number of particles entering the volume across its surface, so that the second term must be identified with the number absorbed within the volume V.

1-2   PARTIAL WAVE AMPLITUDES

If the potential is spherically symmetric and the incident wave has no azimuthal variation, the wave function $\Psi(\mathbf{r})$ is axially symmetric about the direction of incidence $\hat{\mathbf{k}}$. Taking spherical polar coordinates (r,θ,φ), with $\hat{\mathbf{k}}$ as axis and with the center of force as origin, it follows that $\Psi(\mathbf{r})$ is a function of r and θ only and that $\Psi(\mathbf{r})$ can be expanded in a series of Legendre polynomials, which form a complete set in the interval $-1 \le \cos\theta \le +1$,

$$\Psi(r,\theta) = \sum_{\ell=0}^{\infty} r^{-1}f_\ell(r)P_\ell(\cos\theta). \tag{1-19}$$

Each term in this series is an eigenfunction of L^2 and of L_z, where $\mathbf{L}$ is the orbital angular momentum, since

$$L^2 P_\ell (\cos \theta) = [\ell(\ell + 1)\hbar^2] P_\ell (\cos \theta)$$

$$L_z P_\ell (\cos \theta) = 0,$$

where

$$L^2 = - \hbar^2 \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right\}$$

$$L_z = - i\hbar \frac{\partial}{\partial \varphi}.$$

To find the wave equation satisfied by the radial wave function $f_\ell (r)$, the Schrödinger equation is written as

$$[\nabla^2 - U(r) + k^2]\Psi(r,\theta) = 0,$$

where $k^2 = 2mE/\hbar^2$ and $U(r) = 2mV(r)/\hbar^2$. Using the result

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) - \frac{1}{\hbar^2 r^2} L^2,$$

and expansion (1-19), it follows that

$$\sum_{\ell=0}^{\infty} r^{-1} P_\ell (\cos \theta) \left[\frac{d^2}{dr^2} - \frac{\ell(\ell + 1)}{r^2} - U(r) + k^2\right] f_\ell (r) = 0.$$

The radial equation now follows by multiplying by $P_{\ell'} (\cos \theta)$ and integrating over $\cos \theta$, to give

$$\left[\frac{d^2}{dr^2} - \frac{\ell(\ell + 1)}{r^2} - U(r) + k^2\right] f_\ell (r) = 0, \qquad (1-20)$$

where the orthogonality property of the Legendre polynomials has been used

$$\int_{-1}^{+1} P_\ell (\cos \theta) P_{\ell'} (\cos \theta) d \cos \theta = \left(\frac{2}{2\ell + 1}\right) \delta_{\ell\ell'}.$$

For potentials that are not too singular at the origin, so that

$$\lim_{r \to 0} r^{2+\epsilon} |U(r)| < C, \qquad (1-21)$$

the radial function $f_\ell (r)$ can be expanded in a power series

$$f_\ell (r) = \sum_n a_n r^n.$$

An examination of the indicial equation then shows that there are two solutions, one regular at the origin behaving like

$$f_\ell(r) \propto r^{\ell+1},\tag{1-22}$$

and one irregular with

$$f_\ell(r) \propto r^{-\ell}.\tag{1-23}$$

To describe a physical scattering situation, the wave function $\Psi(r)$ must be finite everywhere so that we must choose the regular solution. At sufficiently large r, we may neglect the potential in comparison with k^2, if the potential is of short range[1], and $f_\ell(r)$ will satisfy

$$\left(\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2} + k^2\right)f_\ell(r) = 0.\tag{1-24}$$

Two independent real solutions of this equation are $s_\ell(kr)$ and $c_\ell(kr)$ which are related to the spherical Bessel and Neumann functions[2] $j_\ell(x)$ and $n_\ell(x)$ by $s_\ell(x) = xj_\ell(x)$; $c_\ell(x) = -xn_\ell(x)$. These functions have the properties,

$$s_\ell(x) \underset{x\to0}{\sim} \frac{x^{\ell+1}}{(2\ell+1)!!}, \quad s_\ell(x) \underset{x\to\infty}{\sim} \sin\left(x - \frac{\ell\pi}{2}\right),$$

$$c_\ell(x) \underset{x\to0}{\sim} \frac{(2\ell-1)!!}{x^\ell}, \quad c_\ell(x) \underset{x\to\infty}{\sim} \cos\left(x - \frac{\ell\pi}{2}\right).\tag{1-25}$$

The functions $s_\ell(x)$ and $c_\ell(x)$ can be expressed in terms of polynomials in $(1/x)$ multiplying $\cos x$ and $\sin x$. For $\ell \le 2$, s_i and c_i are

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[1] It can be shown that the following discussion of the asymptotic form of $f_\ell(r)$ applies to all potentials for which $r^{1+\epsilon}V(r) \to 0, \epsilon > 0$ as $r \to \infty$. The Coulomb potential is excluded and will be treated separately.

[2] Morse and Feshbach (1953).

$$s_0(x) = \sin x, \quad c_0(x) = \cos x,$$

$$s_1(x) = \frac{\sin x}{x} - \cos x, \quad c_1(x) = \frac{\cos x}{x} + \sin x,$$

$$s_2(x) = \left(\frac{3}{x^2} - 1\right)\sin x - \frac{3}{x}\cos x, \qquad (1\text{-}26)$$

$$c_2(x) = \left(\frac{3}{x^2} - 1\right)\cos x + \frac{3}{x}\sin x.$$

Sometimes we shall find it convenient to use in place of $s_\ell(x)$ and $c_\ell(x)$, the functions $e_\ell^{\pm}(x)$ defined so that

$$e_\ell^{\pm}(x) = c_\ell(x) \pm is_\ell(x). \qquad (1\text{-}27)$$

For large x, the functions $e_\ell^{\pm}(x)$ have the asymptotic form

$$e_\ell^{\pm}(x) \sim e^{\pm i(x - \ell\pi/2)}. \qquad (1\text{-}28)$$

For large r, $f_\ell(r)$ must have the general form

$$f_\ell(r) \sim f_\ell^A(r),$$

where

$$f_\ell^A(r) = A_\ell\left[s_\ell(kr) + K_\ell c_\ell(kr)\right] \qquad (1\text{-}29a)$$

$$\underset{r \to \infty}{\sim} A_\ell\left[\sin\left(kr - \frac{\ell\pi}{2}\right) + K_\ell\cos\left(kr - \frac{\ell\pi}{2}\right)\right], \qquad (1\text{-}29b)$$

and where A_ℓ and K_ℓ are constants[3]. The A_ℓ are multiplicative normalization constants and the scattering amplitude is

_____

[3] The form (1-29a) holds for values of r for which

$$U(r) \ll k^2 - \ell(\ell + 1)/r^2,$$

while (1-29b) holds for greater values of r for which

$$\ell(\ell + 1)/r^2 \ll k^2.$$

determined by the parameters K_ℓ. To find the connection between the scattering amplitude and K_ℓ the asymptotic part of $\Psi(\mathbf{r})$, which is $\Psi^A(\mathbf{r})$ given by (1.6), can be expanded in Legendre polynomials.

The first term in (1-6), the plane wave $\varphi_k(\mathbf{r})$, has the expansion (Morse and Feshbach, 1953, p. 1466),

$$\varphi_k(\mathbf{r}) = \sum_{\ell=0}^{\infty} (2\ell + 1)i^\ell (kr)^{-1} s_\ell(kr) P_\ell(\cos\theta)$$

and for large r,

$$\varphi_k(\mathbf{r}) \sim \sum_{\ell=0}^{\infty} (2\ell + 1)i^\ell (kr)^{-1} \sin(kr - \frac{\ell\pi}{2}) P_\ell(\cos\theta). \quad (1\text{-}30)$$

The second term in (1-6), representing the outgoing scattered waves, can also be expanded in a series of Legendre polynomials,

$$f_k(\theta)e^{ikr}/r = \left[\sum_{\ell=0}^{\infty} (2\ell + 1)k^{-1}T_\ell P_\ell(\cos\theta) \right] e^{ikr}/r. \quad (1\text{-}31)$$

The coefficients of the expansion, T_ℓ, are called the partial wave scattering amplitudes. From (1-19), (1-30) and (1-31), we see that

$$f_\ell^A(r) \underset{r\to\infty}{\sim} (2\ell + 1)\left[k^{-1}i^\ell \sin\left(kr - \frac{\ell\pi}{2}\right) + k^{-1}T_\ell e^{ikr} \right]. \quad (1\text{-}32)$$

Writing

$$e^{ikr} = e^{i\ell\pi/2}\left\{ \cos\left(kr - \frac{\ell\pi}{2}\right) + i\sin\left(kr - \frac{\ell\pi}{2}\right) \right\}, \quad (1\text{-}33)$$

and comparing with (1-29b), we see that K_ℓ is given in terms of T_ℓ by

$$K_\ell = \frac{T_\ell}{1 + iT_\ell}. \quad (1\text{-}34)$$

In terms of ingoing and outgoing radial waves, $f_\ell^A(r)$ has the asymptotic form, from (1-32),

$$f_\ell^A(r) \sim \frac{-(i)^\ell (2\ell + 1)}{2ik} \left[e^{-i(kr - \ell\pi/2)} - S_\ell(k)e^{+i(kr - \ell\pi/2)} \right],$$

$$(1\text{-}35a)$$

where

$$S_\ell(k) = (2iT_\ell + 1).$$ (1-35b)

The conservation laws discussed in Section 1-1 require that the outgoing radial flux never exceeds the ingoing radial flux. It follows that $S_\ell(k)$ must always satisfy

$$|S_\ell(k)| \le 1.$$ (1-36)

For real potentials, only elastic scattering is possible and the outgoing and ingoing radial fluxes are equal, so that $|S_\ell(k)| = 1$. It follows that $S_\ell(k)$ can be represented as

$$S_\ell(k) = e^{2i\delta_\ell},$$ (1-37)

where δ_ℓ is real constant called the phase shift of order ℓ. In terms of phase shifts, the partial wave scattering amplitude T_ℓ is (from 1-35b)

$$T_\ell = \frac{1}{2i}\left(e^{2i\delta_\ell} - 1\right) = e^{i\delta_\ell}\sin\delta_\ell,$$ (1-38)

and $K_\ell = \tan\delta_\ell$.

S_ℓ is known as an S-matrix or scattering matrix element, and K_ℓ as a reaction matrix element. The complete scattering amplitude $f_k(\theta)$ can be written in terms of the phase shifts (from 1-31), as

$$f_k(\theta) = \sum_{\ell=0}^{\infty} \frac{1}{2ik}\left(e^{2i\delta_\ell} - 1\right)(2\ell + 1)P_\ell(\cos\theta).$$ (1-39)

The total cross section σ then satisfies

$$\sigma = \sum_{\ell=0}^{\infty} \sigma_\ell,$$

where

$$\sigma_\ell = \frac{4\pi}{k^2}(2\ell + 1)\sin^2\delta_\ell.$$ (1-40)

The quantities σ_ℓ are known as partial cross sections and, since $\sin\delta_\ell$ cannot exceed unity, the σ_ℓ satisfy the inequality

$$\sigma_\ell \le \frac{4\pi(2\ell + 1)}{k^2}.$$ (1-41)

The partial wave expansion has succeeeed in reducing
the partial differential equation (1-5) in three variables, to a
system of second order ordinary differential equations, but
this is only useful if the expansion converges and we shall
now discuss this point in a nonrigorous way. If a potential
vanishes beyond a certain distance a, then according to clas-
sical mechanics particles with impact parameters b > a (see
figure 1-2) will not be scattered. The impact parameter is
related to the momentum P and angular momentum L, by

$$b = L/p,$$

and particles with angular momentum,

$$L > pa,$$

are not scattered. Writing $L \simeq \hbar\ell$ and $p = \hbar k$, it is seen that
scattering is expected to be small in angular momentum states
for which

$$\ell > ka.$$ (1-42)
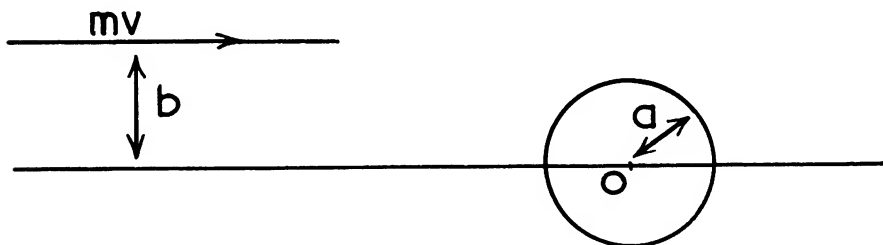
Figure 1-2 Particles with impact parameters b > a are undeflected classically.

When the scattering in a given partial wave is small the
corresponding phase shift is small, and only a finite number
of terms in the partial wave expansion of the scattering ampli-
tude will be important, the number increasing with energy. To
estimate how rapidly the phase shifts decrease with increasing
ℓ, we shall find an integral equation for the reaction matrix
element $K_\ell = \tan \delta_\ell$.

1-3 $^{\ell}$ INTEGRAL EQUATIONS FOR THE PHASE SHIFT

Wronskian relations

Integral equations for the radial wave function and for the phase shift are most easily obtained by considering the Wronskian of two solutions of the radial equations (1-20). Let f_{ℓ} and F_{ℓ} be two solutions of the radial equations for different potentials, $U^{(1)}$ and $U^{(2)}$, but for the same values of k and ℓ. Then f_{ℓ} and F_{ℓ} satisfy the equations,

$$\left(\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2} - U^1(r) + k^2\right) f_{\ell}(r) = 0, \qquad (1\text{-}42a)$$

$$\left(\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2} - U^2(r) + k^2\right) F_{\ell}(r) = 0. \qquad (1\text{-}42b)$$

Multiplying equation (1-42a) by $F_{\ell}(r)$ and equation (1-42b) by $f_{\ell}(r)$ and subtracting, we find

$$F_{\ell}(r)\frac{d^2}{dr^2}f_{\ell}(r) - f_{\ell}(r)\frac{d^2}{dr^2}F_{\ell}(r) = [U^{(1)}(r) - U^{(2)}(r)]f_{\ell}(r)F_{\ell}(r).$$

$$(1\text{-}43)$$

The Wronskian of $f_{\ell}(r)$, $F_{\ell}(r)$ is defined as $W(r)$, where

$$W(r) = F_{\ell}(r)\frac{d}{dr}f_{\ell}(r) - f_{\ell}(r)\frac{d}{dr}F_{\ell}, \qquad (1\text{-}44)$$

and from (1-43), on integrating,

$$W(r) - W(0) = \int_0^r [U^{(1)}(r) - U^{(2)}(r)]f_{\ell}(r)F_{\ell}(r). \qquad (1\text{-}45)$$

If $f_{\ell}(r)$ and $F_{\ell}(r)$ are independent solutions of the same equation, that is if $U^{(1)} = U^{(2)}$, the right hand side of (1-45) vanishes and the Wronskian is independent of r. As an example, we can calculate the Wronskian of $s_{\ell}(x)$ and $c_{\ell}(x)$ from the asymptotic forms of these functions at large r and the result will be correct for all r. We find

$$c_{\ell}(kr)\frac{d}{dr}(s_{\ell}(kr)) - s_{\ell}(kr)\frac{d}{dr}(c_{\ell}(kr)) = k, \qquad (1\text{-}46)$$

and in a similar way

$$e^{\pm}(kr) \frac{d}{dr}(s_\ell(kr)) - s_\ell(kr)\frac{d}{dr}(e^{\pm}(kr)) = k. \qquad (1\text{-}47)$$

Integral equations for the radial wave functions

Using the result (1-46), it is easy to verify by substitution that $f_\ell(r)$ given by

$$f_\ell(r) = s_\ell(kr) + \int_0^\infty g_\ell^P(r,r')U(r')f_\ell(r')dr', \qquad (1\text{-}48)$$

is a solution of the radial equation (1-20), where

$$g_\ell^P(r,r') = -\frac{1}{k}s_\ell(kr_<)c_\ell(kr_>), \qquad (1\text{-}49)$$

and $r_<, r_>$ are the lesser and the greater of r, r' respectively. The solution clearly vanishes at the origin and for large r satisfies the boundary condition

$$f_\ell(r) \sim s_\ell(kr) + K_\ell c_\ell(kr), \qquad (1\text{-}50)$$

with

$$K_\ell = \tan\delta_\ell = -1/k\int_0^\infty s_\ell(kr)U(r)f_\ell(r)dr. \qquad (1\text{-}51)$$

This integral equation for K_ℓ can also be obtained directly from (1-45) by setting $U^{(2)} = 0$, $F_\ell = s_\ell(kr)$ and $U^{(1)} = U$. On the left hand side of (1-45) $W(0) = 0$ and $W(r)$ may be evaluated from the asymptotic forms of the functions.

The function $g_\ell^P(r,r')$ is known as a Green's function. By comparing (1-48) with (1-20), it is seen to satisfy the equation

$$\left(\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2} + k^2\right)g_\ell^P(r,r') = \delta(r - r'). \qquad (1\text{-}52)$$

Different forms of Green's function can be found that allow integral equations incorporating different boundary conditions to be constructed. For example by choosing

$$g_\ell^+(r,r') = -\frac{1}{k}s_\ell(kr_<)e_\ell^+(kr_>) \qquad (1\text{-}53)$$

in place of g_ℓ^P in eq. (1-48), we find solutions satisfying

$$f_\ell^+(0) = 0, \quad f_\ell^+(r) \sim s_\ell(kr) + (k)^{-1} T_\ell e^{i\ell\pi/2} e_\ell^+(kr) \quad (1-54)$$

where the partial wave amplitude T_ℓ has the integral representation

$$T_\ell = e^{i\delta\ell} \sin \delta_\ell = -1/k \int_0^\infty s_\ell(kr) U(r) f_\ell^+(r) dr. \qquad (1-55)$$

Born's approximation

At sufficiently high energy, the functions $c_\ell(kr)$ and $s_\ell(kr)$ will oscillate so rapidly over the interaction region $0 < r < a$, that the integral term in (1-48) will become negligible compared with the first term. We then have

$$f_\ell(r) \simeq s_\ell(kr). \qquad (1-56)$$

Born's approximation for the phase shift is found by using this approximation for $f_\ell(r)$ in the integral equation (1-51):—

$$\tan \delta_\ell \simeq -1/k \int_0^\infty |s_\ell(kr)|^2 U(r) dr. \qquad (1-57)$$

It will be shown that this expression can be used to estimate the phase shifts for large ℓ (any k), from which the convergence of the partial wave series can be confirmed. The incident wave $s_\ell(kr)$ behaves like $(kr)^{\ell+1}$ for small (kr) and then increases exponentially up to a point of inflexion at $(kr) = \sqrt{\ell(\ell+1)}, (\ell \neq 0)$. Beyond this point the function oscillates with roughly unit amplitude. It follows that for sufficiently large ℓ the overlap of the incident wave and the potential in the range $0 < r < a$ can be made as small as we please. Under these conditions the wave function for the ℓth partial wave will be equal to the incident wave to a good approximation and the integral term in (1-48) will be very small. This will occur for values of ℓ roughly given by the condition $(\ell \gg ka)$. The Born approximation (1-57) can now be used to estimate δ_ℓ. Setting $s_\ell(kr) = (kr)^{\ell+1}/(2\ell + 1)!!$ (which is valid for $(kr) \ll \ell$) in (1-57), the approximate phase shift δ_ℓ is

$$\delta_\ell \approx \tan \delta_\ell \simeq - \frac{k^{2\ell+1}}{[(2\ell+1)!!]^2} \int_0^\infty r^{2\ell+2} U(r) dr. \quad (1-58)$$

This expression will be valid only for potentials vanishing for r > a, and for potentials with tails that extend into the region r > a, the Bessel function cannot be approximated in this way. As an example, for the square well potential

$$U(r) = A \quad r < a$$
$$= 0 \quad r > a, \qquad\qquad (1-59)$$

we find

$$\delta_\ell = - \frac{(ka)^{2\ell+1}(a^2 A)}{[(2\ell+1)!!]^2 (2\ell+3)}, \qquad\qquad (1-60)$$

which decreases rapidly with increasing ℓ.

The condition that the overlap of the potential and wave function is small, $\ell \gg ka$, can be satisfied by taking small k, rather than large ℓ, so that (1-58) tells us the behaviour of the phase shifts at low energies, that is

$$\delta_\ell \underset{k \to 0}{\propto} k^{2\ell+1}. \qquad\qquad (1-61)$$

This behaviour is correct for all potentials decreasing faster than a power of r, at large r.

The sign of the phase shift

The Born approximation estimate of the phase shift, given by (1-57), shows that for potentials that do not change sign, the phase shift is positive for an attraction (U negative) and negative for a repulsion (U positive). This is not only true in the Born approximation. From the Wronskian relation, we easily find,

$$\tan \delta_\ell^{(2)} - \tan \delta_\ell^{(1)} = 1/k \int_0^\infty f_\ell(r) F_\ell(r) [U^{(1)}(r) - U^{(2)}(r)] dr, \qquad (1-62)$$

where $\delta_\ell^{(1)}$ is the phase shift of the partial wave $f_\ell(r)$ for scattering by the potential $U^{(1)}$, and $\delta_\ell^{(2)}$ is the phase shift of the partial wave F_ℓ, for scattering by $U^{(2)}$.

If the difference $(U^{(1)} - U^{(2)})$ is small, so that $f_\ell(r)F_\ell(r) \simeq [f_\ell(r)]^2$ we see the sign of the difference $(\delta_\ell^{(2)} - \delta_\ell^{(1)})$ is the same as that of $(U^{(1)} - U^{(2)})$. By constructing a series of comparison potentials between $U^{(1)}$ and $U^{(2)}$, it follows that this result remains true for all $(U^{(1)} - U^{(2)})$. Finally by taking $U^{(2)} = 0$, we establish the result that the phase shift is positive (negative) for attractive (repulsive) potentials.

As an example of the decrease of the phase shifts with increasing ℓ and of the connection between the sign of the potential and the sign of the phase, some results are shown in Table 1-1 for scattering from the potentials

$$U_\pm(r) = \pm 2(1 + 1/r)e^{-2r}. \tag{1-63}$$

Table 1-1

Phase shifts $\delta_\ell^\pm$ for scattering from the potentials $U_\pm(r) = \pm 2(1 + 1/r)e^{-2r}$

(Phase shifts in radians)

k(a.u.)	δ_0^+	δ_1^+	δ_2^+	δ_0^-	δ_1^-	δ_2^-
0.1	-0.058	--	--	0.721	0.0003	--
0.2	-0.1145	-0.0017	--	0.9731	0.0021	--
0.3	-0.1680	-0.0055	--	1.0458	0.0066	--
0.4	-0.2181	-0.0121	-0.0005	1.0575	0.0147	0.0005
0.5	-0.2640	-0.020	-0.0013	1.0448	0.0260	0.0014
0.6	-0.3043	-0.0322	-0.0028	1.0210	0.0406	0.0030
0.8	-0.3713	-0.0584	-0.0082	0.9633	0.0752	0.0087

U_- is the effective potential in atomic units between an electron and the ground state of a hydrogen atom calculated in lowest order, while U_+ is the corresponding potential for positron-hydrogen scattering.

1-4   THE SQUARE WELL AND HARD SPHERE POTENTIALS

The general features of the phase shifts given by the spherical well potential (1-59) for large ℓ, or for small k, are given by the formula (1-60), and we shall next obtain the exact phase shifts for scattering by this potential.

If the potential is attractive (negative), the well depth A can be written as

$$A = -\lambda^2 ,\qquad\qquad (1-64)$$

in which case the radial wave equation becomes for $r < a$,

$$\left(\frac{d^2}{dr^2} - \frac{\ell(\ell + 1)}{r^2} + p^2 \right) f_\ell (r) = 0 , \qquad (1-65a)$$

where

$$p^2 = k^2 + \lambda^2 . \qquad\qquad (1-65b)$$

The solution vanishing at the origin is

$$f_\ell (r) = C_\ell s_\ell (pr) , \ r < a \qquad\qquad (1-66)$$

where C_ℓ is a constant. In the region, $r > a$, the wave function satisfies the equation,

$$\left(\frac{d^2}{dr^2} - \frac{\ell(\ell + 1)}{r^2} + k^2 \right) f_\ell (r) = 0 , \qquad (1-67)$$

for which the general solution is

$$f_\ell^A (r) = s_\ell (kr) + K_\ell c_\ell (kr) , \quad r > a , \qquad (1-68)$$

where K_ℓ is (from equations 1-29a,b) related to the phase shift by

$$K_\ell = \tan \delta_\ell .$$

To determine K_ℓ, we must join $f_\ell (r)$ to $f_\ell^A (r)$ smoothly at $r = a$. To do this, we equate both $f_\ell (r)$ with $f_\ell^A (r)$, and $(df_\ell (r)/dr)$ with $(df_\ell^A (r)/dr)$ at $r = a$, from which we find,

$$C_\ell s_\ell (pa) = s_\ell (ka) + K_\ell c_\ell (ka)$$

$$C_\ell p s_\ell' (pa) = k \{s_\ell' (ka) + K_\ell c_\ell' (ka)\}.$$

In this equation, we have denoted derivatives by primes,

$$s_\ell' (x) \equiv \frac{ds_\ell (x)}{dx}, \quad c_\ell' (x) \equiv \frac{dc_\ell (x)}{dx}.$$

We then find immediately that K_ℓ is given by the equation,

$$K_\ell = \tan \delta_\ell = \left\{ \frac{ks_\ell' (ka)s_\ell (pa) - ps_\ell (ka)s_\ell' (pa)}{pc_\ell (ka)s_\ell' (pa) - kc_\ell' (ka)s_\ell (pa)} \right\}. \quad (1-69)$$

$\underline{\ell = 0}$

In the case for which $\ell = 0$, making use of the relations $s_0(x) = \sin(x)$, $c_0(x) = \cos(x)$, we find

$$K_0 = \left\{ \frac{k \tan (pa) - p \tan (ka)}{p + k \tan (ka) \tan (pa)} \right\}, \quad (1-70)$$

from which

$$\delta_0 = - ka + \tan^{-1} [\frac{k}{p} \tan (pa)].$$

The behavior of the cross section at zero energy is particularly interesting. In general, the ratio $\tan \delta_0 (k)/k$ as $k \to 0$ tends to a finite limit a_s, known as the scattering length,

$$a_s = \lim_{k \to 0} \{\tan \delta_0 (k)\}/k. \quad (1-71)$$

(It should be noted that the scattering length is often defined to be equal to $-a_s$, where a_s is given by (1-71).)

In the present case, we have that

$$a_s = \{\frac{1}{\lambda} \tan (\lambda a) - a\}.$$

In terms of the scattering length, the zero energy cross section for $\ell = 0$ is,

$$\sigma_0 (0) = \lim_{k \to 0} \frac{4\pi \sin^2 \delta_0}{k^2} = 4\pi a_s^2, \quad (1-72)$$

while the zero energy cross section for higher partial waves, vanishes in general. Although a_s is usually finite, exceptions occur if $a\lambda = \tan (\lambda a)$, for which a_s vanishes, or if $(a\lambda)$ is an odd multiple of $(\pi/2)$, for which a_s is infinite. These results are connected with the existence of bound states in the potential

well. If there is a bound state at an energy $-E_B$, then the wave function for $r > a$ is of the form

$$f_0(r) = e^{-\xi r}, \qquad (1-73)$$

where $\xi^2 = 2mE_B/\hbar^2$. This must be joined to the internal wave function (1-65), where p^2 is now $p^2 = \lambda^2 - \xi^2$. The equations joining the solutions in and outside the well are $(\ell = 0)$

$$C_0 \sin (pa) = e^{-\xi a},$$

$$C_0 p \cos (pa) = -\xi e^{-\xi a}.$$

On dividing, we see that ξ is determined by the roots of the equation

$$\frac{1}{p} \tan (pa) = -\frac{1}{\xi}. \qquad (1-74)$$

When the depth of the well is small and

$$(\lambda a) < \frac{\pi}{2},$$

equation (1-74) cannot be satisfied (remembering that $\xi > 0$) and the system has no bound state. Under these circumstances a_S is finite, and if we normalize the phase shift so that $\delta_0(k) \to 0$ as $\lambda \to 0$, we see that $\delta_0(k) \to 0$ as $k \to 0$.
    Increasing λ until (λa) lies in the interval

$$\frac{\pi}{2} < (\lambda a) < \frac{3\pi}{2},$$

we see that equation (1-74) can be satisfied by just one value of ξ and the well supports one bound state. The scattering length a_S remains finite, but in the intermediate case when $(\lambda a) = \pi/2$, we have already seen that a_S is infinite and this implies that $\delta_0(k) \to (\pi/2)$ as $k \to 0$. Since $\delta_0(k)$ for finite k, increases monotonically with λ, it follows that in the interval $\pi/2 < (\lambda a) < 3\pi/2$ $\delta_0(k)$ does not vanish as $k \to 0$, but that

$$\delta_0(k) \to \pi.$$

    Repeating the argument, it is seen that if λ is increased so that the system supports n bound states, then the phase shift satisfies

$$\lim_{k \to 0} \delta_0(k) = n\pi. \tag{1-75a}$$

In the intermediate case in which λ is increased until the $(n + 1)^{th}$ bound state is about to appear and $(a\lambda = (2n + 1)\pi/2)$, we have

$$\lim_{k \to 0} \delta_0(k) = (n + \tfrac{1}{2})\pi. \tag{1-75b}$$

These results turn out to be true generally and are an example of Levinson's theorem, which will be discussed at a later point.

Considered as a function of increasing k, the phase shift δ_0 rises from its threshold value of $(n\pi)$ to maximum, which examination of (1-70) shows is usually less than $(n + 1/2)\pi$, although for certain values of λ and a, the r aximum of δ_0 can be slightly greater than $(n + 1/2)\pi$. As k increases further, δ_0 will decrease and ultimately as $k \to \infty$, $\delta_0 \to 0$. As the energy decreases, the phase shift will pass through the values $(n\pi)$, $(n - 1)\pi$, $(n - 2)\pi$ ... at these energies the total cross section for the $\ell = 0$ partial wave will vanish. In addition, at the energies for which the phase shift takes on the values $(n - 1/2)\pi$, $(n - 3/2)\pi$, ... , the total cross section for the $\ell = 0$ partial wave will attain the maximum possible value of $(4\pi/k^2)$.

Using arguments based on causality, Wigner (1955) has shown that the rate of change of the phase shift with momentum satisfies the inequality

$$\frac{\partial \delta_0(k)}{\partial k} > -a$$

for all interactions with a finite range a. It follows that the rate of decrease of the phase shift through an odd multiple of $(\pi/2)$ cannot be arbitrarily rapid, and that the peak in the cross section must be broad (compared to the energy interval between successive peaks). Such a situation can be termed a broad resonance in contrast to the narrow resonances that can occur when a phase shift <u>increases</u> rapidly through an odd multiple of $(\pi/2)$.

$\ell > 0$

The phase shift for $\ell = 0$, given by equation (1-70), is the sum of a smoothly varying term, $-ka$, and a term

containing tan (pa) which can show rapid variations, as k or
λ changes. The phase shifts for $\ell > 0$, are also the sum of
two terms, which behave in a similar manner. This is seen
most easily if we consider the special case for which (ka) $\gg \ell$.
This allows us to replace the Bessel function $s_\ell(x)$ and
$c_\ell(x)$ by their asymptotic forms for large x, (1–25), and we
find at once that

$$\delta_\ell(k) \approx -(ka - \tfrac{1}{2}\ell\pi) + \tan^{-1}\left[\frac{k}{p}\tan(pa - \tfrac{1}{2}\ell\pi)\right]. \quad (1-76)$$

The phase shift again tends to (nπ) as k → 0 and to zero as
k → ∞, but for small values of k, it is possible for δ_ℓ to
<u>increase</u> rapidly through (n + 1/2)π before decreasing.

Tc discuss the low energy variation of $\delta_\ell(k)$, we can
use equat. ins (1–25) to approximate $\delta_\ell(kr)$ and $s_\ell'(kr)$ for
small k, which gives

$$\tan\delta_\ell \approx \frac{(ak)^{2\ell+1}}{(2\ell + 1)!!(2\ell - 1)!!}\left[\frac{(\ell + 1)s_\ell(pa) - (pa)s_\ell'(pa)}{+(pa)s_\ell'(pa) + \ell s_\ell(pa)}\right].$$

$$(1-77a)$$

If in addition λ is large, (λ $\gg$ k), so that $s_\ell(pa), s_\ell'(pa)$ can
replaced by their asymptotic forms, a good approximation to
$\tan\delta_\ell$ is

$$\tan\delta_\ell \approx \frac{-(ak)^{2\ell+1}}{(a\ell + 1)!!(2\ell -2)!!}\left[\frac{(pa)\cot(pa - \ell\pi/2) - (\ell + 1)}{(pa)\cot(pa - \ell\pi/2) + \ell}\right]$$

$$(1-77b)$$

With the exception of $\ell = 0$, we see that the possi-
bility exists for δ_ℓ to increase rapidly, through an odd
multiple of (π/2) at a value of k for which the denominator
in equation (1–77b) vanishes. If this value of k is k_R, and
remembering that λ $\gg$ k, we can expand $\tan\delta_\ell$ about k = k_R,
to obtain,

$$\tan\delta_\ell \approx \frac{(ak)^{2\ell+1}}{[(2\ell - 1)!!]^2}\frac{1}{b(k^2 - k_R^2)},$$

where

$$b = \frac{\partial}{\partial k^2}\left[pa\ \cot\ \left(pa - \frac{1}{2}\ell\pi\right)\right]_{k=k_R} \approx -\left(\frac{a^2}{2}\right).$$

In terms of the energy, $E = \hbar^2 k^2 / 2m$, we have that

$$\tan \delta_\ell = -\frac{\Gamma(E)}{2(E - E_R)}, \tag{1-78a}$$

where

$$\Gamma(E) = \frac{(ak)^{2\ell+1}}{[(2\ell - 1)!!]^2}\left(\frac{2\hbar^2}{ma^2}\right). \tag{1-78b}$$

Since $\Gamma(E_R)$ is small compared with E_R, we see that $\tan \delta_\ell$ is small and of the order $(\Gamma/2E_R)$ at all energies, except those in a region of width $\Gamma(E_R)$ centered about $E = E_R$, in which the phase shift increases rapidly through an odd multiple of $(\pi/2)$. This behaviour gives rise to a sharp peak in the cross section which we may describe as a narrow resonance. The scattering amplitude T_ℓ has the form

$$T_\ell = e^{i\delta_\ell}\ \sin \delta_\ell = \frac{-\Gamma/2}{(E - E_R) + i\Gamma/2}, \tag{1-79a}$$

and the total cross section for the ℓth partial wave is

$$\sigma_\ell = \frac{\pi}{k^2}\ (2\ell + 1)\left[\frac{\Gamma^2}{(E - E_R)^2 + \Gamma^2/4}\right] \tag{1-79b}$$

This is known as a Breit-Wigner resonance formula, in which the energy E_R is known as the position, and $\Gamma(E_R)$ as the width, of the resonance.

The physical significance of a narrow resonance can be seen if the amplitude C_ℓ of the wave function, $C_\ell s_\ell (pr)$, inside the well is computed. To produce a standard of comparison, we shall normalize the wave outside the well so that it is of unit amplitude,

$$f_\ell(r) \sim \sin\ (kr - \ell\pi/2 + \delta_\ell),\ r \gg a$$

and we then find

$$C_\ell \approx \left(\frac{\hbar^2}{ma}\right) \frac{(ak)^{\ell+1} P_R}{(2\ell - 1)!! \{(E - E_R)^2 + \Gamma^2/4\}^{\frac{1}{2}}} \, . \qquad (1\text{-}80)$$

The amplitude of the wave function inside the well is very small, except near $E = E_R$ when the probability of finding the scattered particle in the well becomes large. At the energy of a narrow resonance, the particle is nearly bound in the well, forming a metastable state. Such states are of great importance in determining the characteristics of atomic and nuclear scattering phenomena and we shall study their properties in some detail in later sections of the book.

The theory of the repulsive square well $(A < 0)$ is left as an exercise for the reader. It may be developed most easily by replacing λ by $i\lambda$ in the formulae that we have obtained.

Hard sphere scattering

Another interesting example is that in which $A \to +\infty$, that is we have an infinite repulsion for $r < a$. The wave function cannot penetrate into the region $r < a$, so the boundary condition that determinates the phase shifts is

$$f_\ell(a) = 0.$$

For $r > a$ we have

$$f_\ell(r) = s_\ell(kr) + \tan \delta_\ell c_\ell(kr),$$

so that

$$\tan \delta_\ell = - \frac{s_\ell(ka)}{c_\ell(ka)} \, . \qquad (1\text{-}81)$$

When $\ell = 0$, this shows that $\delta_0 = -(ka)$, and the scattering cross section at zero energy becomes

$$\sigma(0) = 4\pi a^2 , \qquad (1\text{-}82)$$

which is four times the classical value.

For large k, $(ka \gg \ell)$ we can use the asymptotic forms of the Bessel functions to obtain

$$\delta_\ell \simeq -ka + \ell\pi/2 . \qquad (1\text{-}83)$$

The total cross section is then

$$\sigma(\text{tot}) = \frac{4\pi}{k^2} \sum_{\ell=0}^{\ell_{max}} (2\ell + 1) \sin^2 (-ka + \ell\pi/2). \qquad (1\text{-}84)$$

If we take the maximum value of ℓ in the sum to be (see page 12) $\ell_{max} = ka$, successive terms in the series can be paired, giving

$$\sigma(\text{tot}) = \frac{4\pi}{k^2} \left[\{\sin^2 (ka) + \sin^2 (ka - \pi/2)\} + \right.$$

$$\left. + 2\{\sin^2 (ka - \pi/2) + \sin^2 (ka - 2\pi/2)\} + \ldots \right]$$

$$= \frac{4\pi}{k^2} \sum_{\ell=0}^{\ell_{max}} (\ell) \approx 2\pi a^2. \qquad (1\text{-}85)$$

This is double the classical value, which at first sight would seem contrary to experience. The explanation is that at high energies, half the cross section is concentrated into a narrow diffraction peak in the forward direction.

The differential cross section, in the high energy limit can be shown to be

$$\frac{d\sigma}{d\Omega} = \frac{1}{4} a^2 \left(1 + \cot^2 (\theta/2) \ J_1^2(ka \sin \theta) \right), \qquad (1\text{-}86)$$

where J_1 is the first order Bessel function. For small x, $J_1(x) \simeq x/2$ while for large x it oscillates according to

$$J_1(x) \sim \sqrt{\frac{2}{\pi x}} \ \cos \left(x - \frac{3}{4}\pi \right). \qquad (1\text{-}87)$$

The first term in (1-86) is isotropic and is the same as the classical differential cross section, while the second describes the diffraction scattering, which is concentrated in a peak of angular width $\sim (\pi/ka)$.

1-5   INELASTIC SCATTERING AND THE OPTICAL THEOREM

In section (1-1), we saw that absorption or inelastic scattering can be described by a complex potential. The radial wave function in this case will still be the regular solution of equation (1-20), but the asymptotic form of $f_\ell(r)$ must be modified. When absorption takes place, the outgoing radial flux in each partial wave must be less than the ingoing flux, so that in place of (1.37) we may write

$$S_\ell(k) = \eta_\ell e^{2i\delta_\ell}, \tag{1-90}$$

where η_ℓ the inelasticity, is a real number in the range $0 < \eta < 1$. When no absorption takes place η_ℓ is equal to one. The partial wave scattering amplitude T_ℓ is then represented by

$$T_\ell(k) = \frac{1}{2i}(\eta_\ell e^{2i\delta_\ell} - 1) \tag{1-91}$$

and the complete scattering amplitude $f(\theta)$ is

$$f(\theta) = \sum_{\ell=0}^{\infty} \frac{1}{2ik}(\eta_\ell e^{2i\delta_\ell} - 1)(2\ell + 1)P_\ell(\cos\theta). \tag{1-92}$$

We can define an absorption cross section for the ℓth partial wave as the net ingoing flux divided by the incident flux. The radial current (see (1-13) is for large r,

$$j_r \sim \frac{-\hbar}{2mir^2}\left(f_\ell^* \frac{\partial f_\ell}{\partial r} - f_\ell \frac{\partial f_\ell^*}{\partial r}\right)[P_\ell(\cos\theta)]^2. \tag{1-93}$$

This can be calculated from $f_\ell^A(r)$ given by (1.35), and we find

$$j_r = \frac{\hbar}{4mr^2}\frac{(2\ell+1)^2}{k}(1 - |S_\ell|)^2 = \frac{\hbar}{4mr^2}\frac{1}{k}(1 - \eta_\ell^2)(2\ell+1)^2[P_\ell\cos\theta)]^2. \tag{1-94}$$

The flux absorbed in a sphere of radius r surrounding the scattering center is

$$\int_{(4\pi)} j_r r^2 d\Omega = \frac{\hbar}{mk}\pi(2\ell+1)(1 - \eta_\ell^2).$$

Dividing by the incident flux $F = (\hbar k/m)$ (see 1.12), the absorption cross section $\sigma_\ell(\text{abs})$ is

$$\sigma_\ell(\text{abs}) = \frac{\pi(2\ell + 1)}{k^2}(1 - \eta_\ell^2). \tag{1-95}$$

The elastic scattering cross section for the ℓth partial wave becomes

$$\sigma_\ell(\text{el}) = \frac{4\pi(2\ell + 1)}{k^2}|T_\ell|^2 = \frac{\pi(2\ell + 1)}{k^2}(1 + \eta_\ell^2 - 2\eta_\ell \cos 2\delta_\ell),$$

$$\tag{1-96}$$

and the total cross section for the ℓth partial wave is

$$\sigma_\ell(\text{tot}) = \sigma_\ell(\text{el}) + \sigma_\ell(\text{abs}) = \frac{2\pi(2\ell + 1)}{k^2}(1 - \eta_\ell \cos 2\delta_\ell). \tag{1-97}$$

Several important inequalities are apparent from these expressions:

$$\sigma_\ell(\text{el}) \leq \frac{4\pi(2\ell + 1)}{k^2}, \quad \sigma_\ell(\text{abs}) \leq \frac{\pi(2\ell + 1)}{k^2}, \quad \sigma_\ell(\text{tot}) \leq 4\pi\frac{(2\ell + 1)}{k^2}.$$

$$\tag{1-98a}$$

When the absorption cross section attains its greatest value, the inelasticity parameter η_ℓ must vanish and under these circumstances from (1-96) and (1-97) we see that

$$\sigma_\ell(\text{el}) = \sigma_\ell(\text{abs}) = \frac{1}{2}\sigma_\ell(\text{tot}). \tag{1-98b}$$

It should be noted that the ratio $\sigma_\ell(\text{abs})/\sigma_\ell(\text{el})$ can only become large when both $\sigma_\ell(\text{abs})$ and $\sigma_\ell(\text{el})$ are well below their maximum values.

Examining (1-97) and (1-91) we see that

$$\sigma_\ell(\text{tot}) = \frac{4\pi(2\ell + 1)}{k^2}\text{Im}T_\ell \tag{1-99}$$

and the complete total cross section is

$$\sigma(\text{tot}) = \sum_{\ell=0}^{\infty}\sigma_\ell(\text{tot}) = \sum_{\ell=0}^{\infty}\frac{4\pi(2\ell + 1)}{k^2}\text{Im}T_\ell. \tag{1-100}$$

On the other hand, the forward elastic scattering amplitude is (using $P_\ell(1) = 1$).

$$f_k(0) = \sum_{\ell=0}^{\infty} (2\ell + 1) T_\ell / k, \tag{1-101}$$

and comparing (1-100) and (1-101) we obtain

$$\sigma(\text{tot}) = \frac{4\pi}{k} \text{Im} f_k(0). \tag{1-102}$$

This is the optical theorem. It is a statement of conservation of probability and is valid under all circumstances. In particular, it does not depend on the assumption of a local potential.

1-6   INTEGRAL EQUATIONS FOR THE WAVE FUNCTION

We shall now turn our attention to the problem of finding integral equations for the wave function $\Psi(\mathbf{r})$ and for the scattering amplitude $f_k(\theta)$. Let us start by writing the Schrödinger equation in operator form, using the Dirac notation

$$(H - E) | \Psi(E) \rangle = 0. \tag{1-103}$$

The Hamiltonian can be split into the kinetic energy operator H_0 and the potential energy operator V, so that

$$(H_0 - E) | \Psi(E) \rangle = -V | \Psi(E) \rangle. \tag{1-104}$$

The incident wave $|\varphi_k\rangle$ satisfies the homogeneous equation

$$(H_0 - E) |\varphi_k\rangle = 0, \tag{1-105}$$

so that a formal solution of (1-104) can be written

$$| \Psi(E) \rangle = a |\varphi_k\rangle + G_0(E) V | \Psi(E) \rangle, \tag{1-106}$$

where a is a constant and $G_0(E)$ is the Green's operator or resolvent of $(H_0 - E)$:

$$G_0(E) = \frac{1}{(E - H_0)}. \tag{1-107}$$

The problem then is to construct $G_0(E)$ in the particular representation that we wish to use. Unfortunately, $G_0(E)$ as we have written it is not completely defined. To see this we can express $G_0(E)$ in terms of the eigenvectors $|\varphi_k\rangle$ of H_0.

We shall adopt a normalization for the basis vectors $|\varphi_k\rangle$ that is the same as that of the plane wave function $\varphi_k(\mathbf{r})$ (eq. 1.1),

$$\langle \varphi_{k'} | \varphi_k \rangle = (2\pi)^3 \delta(k - k'), \tag{1-108}$$

with the closure relation

$$\left(\frac{1}{2\pi}\right)^3 \int dk \ |\varphi_k\rangle \langle\varphi_k| = 1. \tag{1-109}$$

The required representation of $G(E)$ is then

$$G_0(E) = \left(\frac{1}{2\pi}\right)^3 \int dk' \ \frac{|\varphi_{k'}\rangle \langle\varphi_{k'}|}{(E - E')}, \tag{1-110}$$

with $E' = (\hbar^2 k'^2 / 2m)$.

As we are interested in positive real E, it is seen that the integration over E' is singular. In general, the resolvent $(H - Z)^{-1}$ of a self-adjoint operator H exists for all complex Z except on the eigenvalue spectrum of H. The eigenvalue spectrum of H_0 consists of all real positive values of E and the singularity in $G_0(E)$ is a branch cut in the interval $0 \le E \le \infty$.

The singularity in the integrand of (1-110) can be avoided, and the integral defined, by adding a small positive or negative imaginary part ϵ to E, and defining $G_0^+(E)$ or $G_0^-(E)$ as the limit $\epsilon \to 0^+$, (a more extended account of the properties of Green's functions can be found in Morse and Feshbach (1953))

$$G_0^{\pm}(E) = \lim_{\epsilon \to 0^+} G_0(E \pm i\epsilon); \ \ G_0(E \pm i\epsilon) = \frac{1}{E \pm i\epsilon - H_0}. \tag{1-111}$$

We have now to find which of the operators G_0^+ or G_0^- to use, and this is determined by imposing the boundary conditions of our problem. There are several ways in which this may be done, and we shall start by giving an argument based on the evolution in time of the state vector. First we define state vectors $|\Psi^{\pm}(E)\rangle$ by using $G_0(E \pm i\epsilon)$ in eq. (1-106). These state vectors are eigenfunctions of energy, with a time dependence of the form $\exp(-iEt/\hbar)$. In a real scattering situation, the wave train is not of infinite duration and we must superimpose solutions to form a wave packet of finite duration. A wave packet $|\Psi^{\pm}(t)\rangle$ may be defined as

$$|\Psi^{\pm}(t)\rangle = \int \rho(E'' - E) |\Psi^{\pm}(E'')\rangle e^{-iE''t/\hbar} dE'', \tag{1-112}$$

where $\rho(x)$ is a function that is zero except for a narrow range of values of x about $x = 0$. The integral equation (1-106) now becomes, using the representation (1-110) for $G_0(E \pm i\epsilon)$

$$|\Psi^{\pm}(t)\rangle = |\varphi(t)\rangle + \int dE'' \int_0^\infty dE'\rho\, (E'' - E)e^{-iE''t/\hbar}$$
$$\frac{|\varphi(E')\rangle\, \langle\varphi\, (E')|\, V|\,\Psi(E'')\rangle}{(E'' \pm i\epsilon - E')} \,, \qquad (1\text{-}113)$$

where the first term describes the incident wave packet, un-
perturbed by the interaction,

$$|\varphi(t)\rangle = a\int \rho(E'' - E)|\varphi(E'')\rangle e^{-iE''t/\hbar}\, dE''. \qquad (1\text{-}114)$$

Provided the interaction is of limited range, the state vector
will at the start of the experiment be identical with the inci-
dent packet $|\varphi(t)\rangle$. As time goes on, the incident packet
will reach the scattering centre and will be modified by the
interaction. The boundary condition we wish to impose is then

$$|\Psi(t)\rangle \xrightarrow[t\to-\infty]{} |\varphi(t)\rangle. \qquad (1\text{-}115)$$

For this to be satisfied the second term in (1-113) has to
vanish at $t \to -\infty$ and the constant a must be set equal to one.
The contributions to the integral over E'' arise from the
singular point at $E'' = E'$. Since $|\Psi(E'')\rangle$ is assumed to be
a well behaved non-singular function of E'', we can set
$E'' = E'$ in this term and take it outside the integral. The
integration then involves the expression.

$$I^{\pm}(t) = \lim_{\epsilon\to 0} \int \frac{e^{-iyt/\hbar}}{y \pm i\epsilon}\, \rho(y + E' - E)\, dy, \qquad (1\text{-}116)$$

where a change of variable from E'' to $y = (E'' - E')$ has been
made. As $t \to \pm\infty$, the infinite oscillations in the exponential
factor ensure that the integral will vanish except at the singu-
lar point $y = 0$ which corresponds to $E' = E''$. To evaluate the
contribution from this point, we may extend the integration
over y to the whole of the real axis, and for $t < 0$ close the
contour by an infinite semicircle in the upper half y plane and
for $t > 0$ by an infinite semicircle in the lower half y plane,
as in figure 1-3.

    For $t < 0$, the pole at $y = i\epsilon$ is included in the contour,
and that at $y = -i\epsilon$ is excluded, and by Cauchy's theorem

$$\lim_{t\to-\infty} I^+(t) = 0; \quad \lim_{t\to-\infty} I^-(t) = 2\pi i\rho(E' - E). \qquad (1\text{-}117a)$$

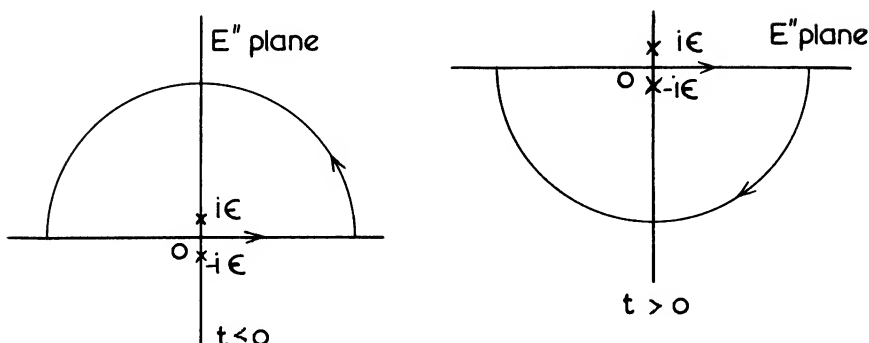For $t > 0$, the pole at $y = -i\epsilon$ is included in the contour and

Figure 1-3   Contours for the evaluation of singular integrals.

that at $y = +i\epsilon$ excluded, giving[4]

$$\lim_{t\to+\infty} I^+(t) = -2\pi i \rho(E' - E); \quad \lim_{t\to+\infty} I^-(t) = 0. \qquad (1-117b)$$

Thus it is the solution $|\Psi^+(t)\rangle$ that satisfies the boundary condition, as it coincides with the incident packet as $t \to -\infty$. We have that

$$\lim_{t\to-\infty} |\Psi^+(t)\rangle = |\varphi(t)\rangle,$$

$$(1-118)$$

$$\lim_{t\to+\infty} |\Psi^+(t)\rangle = |\varphi(t)\rangle - 2\pi i \int \rho(E'-E) e^{-iE't/\hbar} |\varphi(E')\rangle \langle \varphi(E')|V|\Psi^+(E')\rangle dE'.$$

---

[4] These results show that we can write formally

$$\lim_{t\to\infty} \frac{e^{-iyt}}{y - i\epsilon} = 0, \quad \lim_{t\to-\infty} \frac{e^{-iyt}}{y - i\epsilon} = 2\pi i \delta(y),$$

$$\lim_{t\to\infty} \frac{e^{-iyt}}{y + i\epsilon} = -2\pi i \delta(y), \quad \lim_{t\to-\infty} \frac{e^{-iyt}}{y + i\epsilon} = 0.$$

Later we shall be interested in the solution $|\Psi^-(t)\rangle$. This is a solution which coincides with the unperturbed packet in the infinite future:

$$\lim_{t \to +\infty} |\Psi^-(t)\rangle = |\varphi(t)\rangle. \tag{1-119}$$

Green's functions in configuration space

The method of specifying which of the Green's operations G_0^+ or G_0^- satisfy the physical scattering boundary conditions that we have given is rather general and will be useful to us later. We shall now return to the position representation. The wave equation is (1-5)

$$\frac{-2m}{\hbar^2}(H_0 - E)\Psi(r) = (\nabla^2 + k^2)\Psi(r) = U(r)\Psi(r). \tag{1-120}$$

The integral equation for $\Psi^\pm(r)$ is of the form

$$\Psi^\pm(r) = \varphi_k(r) + \int G_0^\pm(r,r')U(r')\Psi^\pm(r')dr', \tag{1-121}$$

where $\varphi_k(r)$ is the incident plane wave (1-1). In order that $\Psi^\pm(r)$ should satisfy the Schrödinger equation, it can be seen by substitution that the Green's function $G_0^\pm(r,r')$ must be a solution of the equation

$$(\nabla^2 + k^2)G_0^\pm(r,r') = \delta(r - r'). \tag{1-122}$$

Apart from a factor $(2m/\hbar^2)$, $G_0^\pm(r,r')$ is just the matrix element of $G_0^\pm(E)$, and from (1-111),

$$G_0^\pm(r,r') = \frac{\hbar^2}{2m}\langle r|G_0^\pm(E)|r'\rangle. \tag{1-123}$$

Using (1-110),

$$G_0^\pm(r,r') = +\left(\frac{1}{2\pi}\right)^3 \int dk' \frac{\langle r|\varphi_k'\rangle\langle\varphi_k'|r'\rangle}{(k^2 + i\epsilon - k'^2)}. \tag{1-124}$$

The wave functions $\langle r|\varphi_k\rangle$ are the plane waves $\varphi_k(r)$, where

$$\langle r|\varphi_k\rangle \equiv \varphi_k(r) = e^{ik\cdot r},$$

from which

$$G_0^{\pm}(\mathbf{r},\mathbf{r}') = \left(\frac{1}{2\pi}\right)^3 \int d\mathbf{k}' \left\{\frac{\exp\left(i\mathbf{k}'\cdot(\mathbf{r}-\mathbf{r}')\right)}{(k^2 \pm i\epsilon - k'^2)}\right\}. \quad (1\text{-}125)$$

The same expression can be found directly from (1-122), by expanding $G_0^{\pm}(\mathbf{r},\mathbf{r}')$ as $G_0^{\pm}(\mathbf{r},\mathbf{r}') = \int d\mathbf{k}\, a(\mathbf{k}) \exp(i\mathbf{k}r)$, and determining $a(\mathbf{k})$ by inserting this expression in (1-122).

We shall first treat the case of G_0^+. The integral is easily evaluated using contour integration. In spherical polar coordinates (k, θ, φ):

$$\int d\mathbf{k}' = \int_0^{2\pi} d\varphi \int_{-1}^{1} d(\cos\,\theta) \int_0^{\infty} k'^2 dk' ,$$

from which, on integrating over φ and θ,

$$G_0^+(\mathbf{r},\mathbf{r}') = \frac{1}{4\pi^2} \int_0^{\infty} k' \frac{e^{ik'R} - e^{-ik'R}}{iR(k^2 + i\epsilon - k'^2)} dk' , \quad (1\text{-}126)$$

where $R = |\mathbf{r} - \mathbf{r}'|$. The integrand is an even function of k' so the integral can be extended over the whole of the real axis, giving

$$G_0^+(\mathbf{r},\mathbf{r}') = \frac{1}{8\pi^2}\frac{1}{iR} \int_{-\infty}^{\infty} e^{ik'R}\left[\frac{1}{k + i\epsilon - k'} - \frac{1}{k + i\epsilon + k'}\right] dk' .$$

The integrand vanishes exponentially as $\mathrm{Im}\,k' \to \infty$ and the integral can be closed by an infinite semi-circle in the upper half k' plane. Using Cauchy's theorem, the first term in square brackets makes the contribution,

$$\int_{-\infty}^{\infty} \frac{e^{ik'R}}{k + i\epsilon - k'} dk' = -2\pi i e^{ikR}.$$

The pole in the second term in square brackets at $k' = -k - i\epsilon$ is excluded from the contour and makes no contribution. The final result is

$$G_0^+(\mathbf{r},\mathbf{r}') = \frac{-1}{4\pi} R^{-1} e^{ikR}. \quad (1\text{-}127a)$$

In just the same way we can find G_0^- which is

$$G_0^-(\mathbf{r},\mathbf{r}') = \frac{-1}{4\pi} R^{-1} e^{-ikR}. \quad (1\text{-}127b)$$

From the analysis of the time dependence of the wave function, we expect the integral term in the equation for Ψ^+ to represent scattered outgoing spherical waves, which is the correct boundary condition for physical scattering. For large $|r|$ we have that

$$\frac{e^{ikR}}{R} \to \frac{1}{r} e^{ikr} e^{-ikr' \cos \alpha}$$

where α is the angle between r and r'. The asymptotic form of $\Psi^+(r)$ is then

$$\Psi^+(r) \sim e^{ik \cdot r} + f_k^+(\theta) e^{ikr}/r, \tag{1-128}$$

where the scattering amplitude $f_k^+(\theta)$ is[5]

$$f_k^+(\theta) = -\frac{1}{4\pi} \int e^{-ik' \cdot r'} U(r') \Psi^+(r') dr' \tag{1-129}$$

$$= -\frac{1}{4\pi} (\varphi_{k'}, U\Psi^+) = -\frac{1}{4\pi}\left(\frac{2m}{\hbar^2}\right) \langle \varphi_{k'} | V | \Psi^+ \rangle,$$

where k' is a vector in the direction of r, and of magnitude $|k'| = |k|$ so that $kr' \cos \alpha = k' \cdot r'$.

The solution $\Psi^-(r)$ has the asymptotic form

$$\psi^-(r) \sim e^{ik \cdot r} + f_k^-(\theta) e^{-ikr}/r, \tag{1-130}$$

with

$$f_k^-(\theta) = -\frac{1}{4\pi} \int e^{+ik' \cdot r} U(r) \Psi_k^-(r) d(r) = -\frac{1}{4\pi} (\varphi_{-k'}, U\Psi^-). \tag{1-131}$$

---

[5] The notation (φ, Ψ) is employed to denote the scalar product of two wave functions. In the position representation for a single particle problem

$$(\varphi, \Psi) = \int dr \varphi^*(r) \Psi(r).$$

The scalar product has the same value in all representations, so in terms of Dirac's bra and ket vectors $\langle \varphi_k |$ and $| \Psi^+ \rangle$, we have

$$-4\pi f_k^+(\theta) = \langle \varphi_{k'} | U | \Psi^+ \rangle.$$

It corresponds to an incident plane wave, but an incoming
rather than outgoing spherical wave. From the boundary con-
ditions (1-128), (1-130) we see that

$$\Psi_{\mathbf{k}}^{-}(\mathbf{r}) = [\Psi_{-\mathbf{k}}^{+}(\mathbf{r})]^{*},$$

where the wave functions are labeled by the incident wave
vectors $\mathbf{k}$, or $-\mathbf{k}$.

Time reversal invariance

To interpret the solution $\Psi^{-}(\mathbf{r})$ further, we notice that
if the Hamiltonian does not depend on time and is real, the
Schrödinger equation is invariant under the combined operations
of $t \to -t$ and complex conjugation. This combined operation is
known as time reversal. Under these circumstances if $\Psi(t)$
satisfies

$$H\Psi(t) = i\hbar \frac{\partial \Psi}{\partial t}, \tag{1-132}$$

then so does the wave function $\Psi_T(t) \equiv \Psi^{*}(-t)$. The wave func-
tion Ψ_T is known as the time reversed wave function. It is
clear that under the time reversal operation, the momentum and
position vectors behave like

$$\mathbf{k} \to -\mathbf{k}$$
$$\mathbf{r} \to \mathbf{r} \tag{1-133}$$

and the angular momentum vector $\mathbf{J}$, like $\mathbf{J} \to -\mathbf{J}$.

It follows that the time reversed wave function corres-
ponding to $\Psi_{\mathbf{k}}^{+}(\mathbf{r})$ is $[\Psi_{-\mathbf{k}}^{+}(\mathbf{r})]^{*}$ which is the same as $\Psi_{\mathbf{k}}^{-}(\mathbf{r})$.
The scattering amplitudes $f_{\mathbf{k}}^{+}(\theta)$ and $f_{\mathbf{k}}^{-}(\theta)$ are then connected,
using an obvious notation, by

$$[f^{+}(\mathbf{k} \to \mathbf{k}')]^{*} = f^{-}(-\mathbf{k}' \to -\mathbf{k}). \tag{1-134}$$

The amplitude $[f_{\mathbf{k}}^{+}]^{*}$ describes scattering from $\mathbf{k}$ to $\mathbf{k}'$ and
$f_{\mathbf{k}}^{-}$ describes scattering from $-\mathbf{k}'$ to $-\mathbf{k}$, which is the time
reversed situation.

The partial wave Green's functions

The Green's functions g_ℓ^+ introduced earlier (1-53) are just the coefficients of the expansion of G_0^+ in Legendre polynomials. Using the expansion (Morse and Feshbach, 1953, p. 1466)

$$\frac{e^{ikR}}{R} = \sum_{\ell=0}^{\infty} (2\ell + 1)ikj_\ell(kr_<)h_\ell(kr_>)P_\ell(\cos\theta), \quad (1-135)$$

where $h_\ell(r) = ij_\ell(r) - n_\ell(r)$ and θ is the angle between $\mathbf{r}$ and $\mathbf{r}'$, it follows that

$$G_0^+(\mathbf{r},\mathbf{r}') = \sum_{\ell=0}^{\infty} \left(\frac{2\ell + 1}{4\pi rr'}\right)g_\ell^+(r,r')P_\ell(\cos\theta). \quad (1-136)$$

The Green's function $G_0^P(\mathbf{r},\mathbf{r}') = 1/2[G_0^+(\mathbf{r},\mathbf{r}') + G_0^-(\mathbf{r},\mathbf{r}')]$ is real and the coefficients in the Legendre polynomial expansion of this function are the Green's functions $g_\ell^P(r,r')$ (1-49), which generate the standing wave solutions of the radial equations,

$$G_0^P(\mathbf{r},\mathbf{r}') = \sum_{\ell=0}^{\infty} \left(\frac{2\ell + 1}{4\pi rr'}\right)g_\ell^P(r,r')P_\ell(\cos\theta). \quad (1-137)$$

The Born approximation

The Born approximation for the scattering amplitude is found by substituting the incident wave for the exact wave function on the right hand side of (1-129),

$$-4\pi f^B(\theta) = \int e^{-i\mathbf{k}'\cdot\mathbf{r}} U(r)e^{i\mathbf{k}\cdot\mathbf{r}} d\mathbf{r}. \quad (1-138)$$

This will be justified if the difference $|e^{i\mathbf{k}\cdot\mathbf{r}} - \Psi^+(\mathbf{r})|$ is small over the range where U is large. From our discussion in section 1-3, this difference is seen to be small provided that the phase shifts δ_ℓ are small for all ℓ. The critical case is $\ell = 0$ and from (1-57) the condition is seen to be

$$\left(\frac{a\bar{U}}{k}\right) \ll 1, \quad (1-139)$$

where $\overline{U}$ is the average depth of the potential well.[6] The condition is sufficient, but is too restrictive, for example it will not work for small k, and under some circumstances the Born approximations can be accurate at all energies. To obtain another condition valid for all k, we may estimate $|\Psi^+(\mathbf{r}) - e^{i\mathbf{k}\cdot\mathbf{r}}| \equiv I(\mathbf{r})$ by substituting the incident plane wave into the right hand side of (1.120),

$$I(\mathbf{r}) = -\frac{1}{4\pi}\int \frac{e^{ikR}}{R} U(\mathbf{r}')e^{i\mathbf{k}\cdot\mathbf{r}'} d\mathbf{r}' ,$$

where $\mathbf{R} = \mathbf{r}' - \mathbf{r}$. Changing the variable of integration to $\mathbf{R}$ we have immediately

$$|I(\mathbf{r})| = \frac{1}{4\pi}|\int R^{-1} e^{i(kR+\mathbf{k}\cdot\mathbf{R})} U(|\mathbf{r}+\mathbf{R}|)d\mathbf{R}| \leq \frac{1}{4\pi}|\int R^{-1} U(|\mathbf{r}+\mathbf{R}|)d\mathbf{R}|.$$

The value of the integral is approximately $a^2\overline{U}$, so a sufficient condition for the Born approximation to be accurate at all energies is

$$|a^2\overline{U}| \ll 1. \tag{1-140}$$

By examining eq. (1-75) we see that in the case of the square well, this is the condition for the potential to be too weak to support a bound state, and in fact it can be shown generally that if bound states are absent, the Born approximation will converge.

In terms of the momentum transfer $\hbar\mathbf{K}$, where $\mathbf{K} = \mathbf{k} - \mathbf{k}'$, the scattering amplitude in the Born approximation is

$$f^B(\theta) = -\frac{1}{4\pi}\int e^{i\mathbf{K}\cdot\mathbf{r}} U(\mathbf{r})d\mathbf{r}, \tag{1-141}$$

and it is seen that the Born approximation is proportional to the Fourier transform of the potential. The Fourier transform of a potential well of range a can only be large for values of K such that

---

[6] As $U = (2m/\hbar^2)V$ and $k = mv/\hbar$, the condition (1-139) can be written as $[2a\overline{V}/\hbar v] \ll 1$. In this form, it is clear that the domain of validity of Born's approximation depends only on the velocity v of the incident particle and not on its mass or energy.

$$K \lesssim \frac{1}{a}$$

and it follows, on expressing K in terms of the scattering angle θ, $K = 2k \sin \theta/2$, that at high energies, where the Born approximation is valid, the scattering is confined to the forward direction, within the cone with

$$\theta \lesssim \frac{1}{ka} . \tag{1-142}$$

As an example, we may again take the zero order or static interaction between an electron and a hydrogen atom (1-63). On performing the integration (1-141) we find (in atomic units)

$$\left| f^B(\theta) \right|^2 = \frac{4(8 + K^2)^2}{(4 + K^2)^4} = \frac{(2 + k^2 \sin^2 (\theta/2))^2}{4(1 + k^2 \sin^2 (\theta/2))^4} . \tag{1-143}$$

This is expected to be accurate at energies over a hundred electron volts, and is strongly peaked in the forward direction. For large k^2, it is easy to show that the total cross section

$$\sigma = 2\pi \int \left| f^B(\theta) \right|^2 d(\cos \theta) \tag{1-144}$$

is proportional to $1/E$, where E is the incident energy.

The Born expansion

If the integral equation (1-121) is written in operator form as in (1-106)

$$\left| \Psi^+ \right\rangle = \left| \varphi_k \right\rangle + G_0^+ (E) V \left| \Psi^+ \right\rangle , \tag{1-145}$$

a further equation can be obtained by substituting $\left| \varphi \right\rangle + G_0^+ V \left| \Psi^+ \right\rangle$ for $\left| \Psi^+ \right\rangle$ on the right hand side:—

$$\left| \Psi^+ \right\rangle = \left| \varphi_k \right\rangle + G_0^+ V \left| \varphi_k \right\rangle + G_0^+ V G_0^+ V \left| \Psi^+ \right\rangle . \tag{1-146}$$

Repeating this iterative process, an infinite series for $\left| \Psi^+ \right\rangle$ can be obtained

$$\left| \Psi^+ \right\rangle = (1 + G_0^+ V + G_0^+ V G_0^+ V + \ldots) \left| \varphi_k \right\rangle . \tag{1-147}$$

The scattering amplitude can also be expanded by substituting this series for $\left| \Psi^+ \right\rangle$ on the right hand side of (1-129),

$$f_{\mathbf{k}}(\theta) = -\frac{1}{4\pi}\left(\frac{2m}{\hbar^2}\right) \langle \varphi_{\mathbf{k}'}|V|\Psi^+\rangle \tag{1-148a}$$

$$= -\frac{1}{4\pi}\left(\frac{2m}{\hbar^2}\right) \langle \varphi_{\mathbf{k}'}|V + VG_0^+V + VG_0^+VG_0^+V + \ldots|\varphi_{\mathbf{k}}\rangle, \tag{1-148b}$$

where we have labeled the incident state as $|\varphi_{\mathbf{k}}\rangle$ and final state as $|\varphi_{\mathbf{k}'}\rangle$. The amplitude $f_{\mathbf{k}}$ can be written as

$$-\left(\frac{2\pi\hbar^2}{m}\right)f_{\mathbf{k}}(\theta) = T_{\mathbf{k}',\mathbf{k}} = \langle \varphi_{\mathbf{k}'}|V + VG^+V|\varphi_{\mathbf{k}}\rangle, \tag{1-149}$$

where

$$G^+ = G_0^+ + G_0^+VG_0^+ + \ldots. \tag{1-150}$$

Comparing (1-148a) and (1-149), we see that G^+ is also a Green's function, with the property

$$|\Psi^+\rangle = |\varphi_{\mathbf{k}}\rangle + G^+V|\varphi_{\mathbf{k}}\rangle. \tag{1-151}$$

From the Schrödinger equation

$$(H - E)|\Psi^+\rangle = 0, \quad H = H_0 + V,$$

we see that G^+ is the resolvent of the <u>total</u> Hamiltonian H

$$G^+(E) = \lim_{\epsilon \to 0^+} \frac{1}{E + i\epsilon - H}. \tag{1-152}$$

The operator $(V + VG^+V)$ is known as the transition operator, $t(E)$,

$$t(E) \equiv V + VG^+(E)V, \tag{1-153a}$$

in which case the transition matrix is given in terms of $t(E)$ by

$$T_{\mathbf{k}',\mathbf{k}} = \langle \varphi_{\mathbf{k}'}|t(E)|\varphi_{\mathbf{k}}\rangle. \tag{1-153b}$$

The convergence of series such as (1-147) or (1-150) is by no means guaranteed. The conditions under which the series for the Green's function G^+ converges has been investigated for a wide class of potentials by Klein and Zemach (1958), and the Born expansions of the partial wave amplitudes have been discussed by Kohn (1952), Jost and Pais (1951) and Manning (1965). In general terms (we refer the reader to the

original papers for the precise conditions), it can be said that the Born series always converges at sufficiently high energies, provided the potential satisfies the conditions.

$$\int |r - r'|^{-1} V(r') dr' < C \quad \text{all } r,$$

$$\int |r - r'|^{-1} V(r') dr' \sim 0\left(\frac{1}{r}\right) \quad \text{as } r \to \infty.$$

For the Born expansion to be convergent at all energies requires conditions to be satisfied that are equivalent to demanding that the potential possesses no bound states.

The momentum representation

It is often useful to represent the integral equation (1-145) in momentum space, rather than in configuration space, because the Green's function G_O is diagonal in this representation. The unperturbed states are described by a wave function $\Phi_k(q)$, where

$$\Phi_k(q) = \langle q | \varphi_k \rangle = \left(\frac{1}{2\pi}\right)^{3/2} \int e^{-iq \cdot r} \varphi_k(r) dr = (2\pi)^{3/2} \delta(k - q).$$

$$(1-154)$$

The wave functions $\Phi_k(q)$ satisfy the closure relation (compare 1-109)

$$(2\pi)^{-3} \int dk \, \Phi_k^*(q) \Phi_k(q') = \delta(q' - q),$$

and the Green's function for the operator $(H_0 - E)$ in the momentum representation $G_0(q, q')$ is

$$G_0^{\pm}(q, q') = \frac{\hbar^2}{2m} \langle q | G_0^{\pm} | q' \rangle = \frac{\delta(q - q')}{k^2 \pm i\epsilon - q^2}. \qquad (1-155)$$

The integral equation for the momentum space wave function $\Psi_{\pm}(q) = \langle q | \Psi_{\pm} \rangle$ becomes

$$\Psi^{\pm}(q) = \Phi_k(q) + \frac{1}{k^2 \pm i\epsilon - q^2} \int \widetilde{U}(q - q') \Psi_k^{\pm}(q') dq', \quad (1-156)$$

where $\widetilde{U}(q)$ is the Fourier transform of the potential $U(r)$

$$\widetilde{U}(q) = (2\pi)^{-3/2} \int dr \, e^{-iq \cdot r} U(r). \qquad (1-157)$$

From (1-129) the scattering amplitude can be written as

$$-4\pi f_{\mathbf{k}}^{+}(\theta) = \int d\mathbf{q} \int d\mathbf{q'} \langle \varphi_{\mathbf{k'}} | \mathbf{q} \rangle \langle \mathbf{q} | U | \mathbf{q'} \rangle \langle \mathbf{q'} | \Psi_{\mathbf{k}}^{+} \rangle,$$

from which

$$-4\pi f_{\mathbf{k}}^{+}(\theta) = \int d\mathbf{q'} \widetilde{U}(\mathbf{k'} - \mathbf{q'}) \Psi_{\mathbf{k}}^{+}(\mathbf{q'}). \qquad (1\text{-}158)$$

To recover the Born approximation, we substitute the incident wave $(2\pi)^{3/2} \delta(\mathbf{k} - \mathbf{q})$ for $\Psi_{\mathbf{k}}^{+}(\mathbf{q'})$ in (1-155), giving

$$-4\pi f_{\mathbf{k}}^{B}(\theta) = (2\pi)^{3/2} \widetilde{U}(|\mathbf{k'} - \mathbf{k}|), \qquad (1\text{-}159)$$

which agrees with (1-138).

1-7   SOME ANALYTIC PROPERTIES OF THE PARTIAL WAVE AMPLITUDES

Many results of interest have come from the study of scattering amplitudes as a function of complex k or E.[7]   We shall study the partial wave amplitudes for the large class of potentials that can be represented by a superposition of exponentials,

$$U(r) = \int_{\mu}^{\infty} c(a) e^{-\alpha} d\alpha. \qquad (1\text{-}160)$$

The radial wave functions $f_{\ell}(r)$ are functions of k as well as r, and we shall write them in this section as $f_{\ell}(k,r)$. They satisfy, as before, the equation

$$\left(\frac{d^2}{dr^2} - \frac{\ell(\ell + 1)}{r^2} - U(r) + k^2 \right) f_{\ell}(k,r) = 0. \qquad (1\text{-}161)$$

From our earlier discussion in section (1-2), we know that an arbitrary solution of this equation will be asymptotic, for large r, to a combination of the functions $s_{\ell}(kr)$ and $c_{\ell}(kr)$ or, alternatively, to a combination of the functions

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[7]An extensive account of the analytic properties of scattering amplitudes can be found in a book by de Alfaro and Regge (1965).

$e_\ell^\pm(kr)$. For large (kr) the functions $e^\pm(kr)$ have the form (equation 1-28) $\exp \pm i(kr - \ell\pi/2)$ and it is therefore possible to define solutions $f_\ell^\pm(k,r)$ of the radial equation that satisfy the boundary condition

$$f_\ell^\pm(k,r) \sim \exp[\pm i(kr - \ell\pi/2)].$$

We now introduce a new function $\varphi_\ell(k,r)$ by requiring that

$$f_\ell^+(k,r) = \varphi_\ell(-k,r)\exp[+i(kr - \ell\pi/2)],$$

$$f_\ell^-(k,r) = \varphi_\ell(+k,r)\exp[-i(kr - \ell\pi/2)], \qquad (1\text{-}162)$$

where, to satisfy the boundary condition, we must have that

$$\lim_{r\to\infty} \varphi_\ell(\pm k,r) = 1. \qquad (1\text{-}163)$$

At the origin, the functions $f_\ell^\pm(k,r)$, which are linear combinations of the regular and irregular solutions of the equation, must be proportional to $(kr)^{-\ell}$. This allows us to define coefficients $\varphi_\ell(\pm k)$, called Jost functions as

$$\varphi_\ell(\pm k) = \lim_{r\to 0} \frac{(\pm kr)^\ell f_\ell^\mp(k,r)}{(2\ell + 1)!!} . \qquad (1\text{-}164a)$$

In terms of the functions $\varphi_\ell(k,r)$, this definition becomes

$$\varphi_\ell(\pm k) = \lim_{r\to 0} \frac{i^\ell(\pm kr)^\ell \varphi_\ell(\pm k,r)}{(2\ell + 1)!!} . \qquad (1\text{-}164b)$$

It is now possible to find the combination of the functions $f_\ell^+(k,r)$ and $f_\ell^-(k,r)$ that is regular at the origin. Calling the regular solution $f_\ell^R(k,r)$ we have that

$$f_\ell^R(k,r) = \left[(-1)^\ell \varphi_\ell(-k)f_\ell^-(k,r) - \varphi_\ell(+k)f_\ell^+(k,r)\right], (1\text{-}165)$$

and this will behave like r^ℓ at the origin.

Comparing the asymptotic form of this solution with (1-35), it is seen that the S-matrix element $S_\ell(k)$ can be written as

$$S_\ell(k) = \frac{\varphi_\ell(k)}{\varphi_\ell(-k)} . \tag{1-166}$$

In what follows, the case of $\ell = 0$ will be treated, following the method of Martin (1965), but similar results for $\ell > 0$ can be obtained. By inserting (1-162a) into the Schrödinger equation, an equation for $\varphi_0(k,r)$ is obtained:—

$$\left[\frac{d^2}{dr^2} - 2ik \frac{d}{dr} - U(r) \right] \varphi_0(k,r) = 0. \tag{1-167}$$

As the potential is a superposition of exponentials, we attempt to write $\varphi_0(k,r)$ in a similar form

$$\varphi_0(k,r) = 1 + \int_0^\infty \rho_k(a) e^{-ar} da. \tag{1-168}$$

The insertion of this expression for $\varphi_0(k,r)$ into the equation (1-167), with the use of (1-160), leads to an integral equation for $\rho_k(a)$

$$a(a + 2ik)\rho_k(a) = c(a) + \int_0^a c(a-\beta)\rho_k(\beta)d\beta. \tag{1-169}$$

As $c(a)$ vanishes for $a < \mu$ (see 1-160), the lower limit on the integral in this equation must be μ rather than zero, and the upper limit $(a - \mu)$ rather than a, and

$$a(a + 2ik) \rho_k(a) = c(a) + \int_\mu^{a-\mu} c(a-\beta)\rho_k(\beta)d\beta. \tag{1-170}$$

We now see that $\rho_k(a)$ must also vanish for $a < \mu$ and the lower limit of integration in (1-168) is in fact μ. Equation (1-170) can now be solved by iteration, because if $\rho_k(a)$ is known for $a < n\mu$, it may be inserted on the right hand side of (1-170), giving, on the left hand side, $\rho_k(a)$ in the range $a < (n + 1)\mu$. For example

$$\rho_k(a) = \frac{c(a)}{a(a + 2ik)} \qquad \mu \leq a < 2\mu$$

$$= \frac{1}{a(a + 2ik)} \left[\rho c(a) + \int_{\mu}^{a-\mu} \frac{c(a - \beta)c(\beta)}{\beta(\beta + 2ik)} \, d\beta \right], \quad 2\mu < a < 3\mu$$

$$= \ldots .$$

This iterative procedure can be carried out for all complex values of k except for values of k which make $(a + 2ik)$ vanish. That is except for values of k on the positive imaginary axis with $|k| > \mu/2$.

It is now necessary to check whether a finite $\rho_k(a)$ exists. To do this we consider all values of k, except those on the line where $(a + 2ik)$ vanishes, by requiring

$$|a + 2ik| > a \sin \epsilon$$
$$|a + 2ik| > 2|k| \sin \epsilon, \tag{1-171}$$

where ϵ is as small as we please. Let us also introduce a positive increasing function $B(a)$ such that

$$|c(a)| < B(a). \tag{1-172}$$

Then from (1-170)

$$|\rho_k(a)| < \frac{B(a)}{a^2 \sin \epsilon} \left[1 + \int_{\mu}^{a} |\rho_k(\beta)| \, d\beta \right].$$

Differentiating we find

$$\frac{d}{da} \frac{|\rho_k(a)|}{y(a)} < \frac{|\rho_k(a)|}{y(a)} \cdot y(a),$$

with $y(a) \equiv B(a)/a^2 \sin \epsilon$, from which we easily find that

$$|\rho_k(a)| < \frac{B(a)}{a^2 \sin^2 \epsilon} \exp\left[\int_{\mu}^{a} \frac{B(\beta)}{\beta^2 \sin^2 \epsilon} \, d\beta \right]. \tag{1-173}$$

If we can find a function, $B(a)$, such that

$$\int_{\mu}^{a} (B(\beta)/\beta^2) d\beta \tag{1-174}$$

exists, it follows that $\rho_k(a)$ exists everywhere except on the excluded line. Equation (1-170) then shows that $\rho_k(a)$ and hence $\varphi(k, r)$ are analytic functions of k, again with the

exception of the excluded line. Further investigation shows that the excluded line is a branch cut, and that as $|k| \to \infty$ in any direction, $|\varphi_0(k,r) - 1| \to 0$.

The condition (1-174) is satisfied with $B(a) = a^{1-n}, n > 0$ and potentials for which $|c(a)| < a^{1-n}$ are those which are less singular than $1/r^2$ at the origin. For potentials which are not expressible in the form (1-160), Bargmann (1949) has shown that φ_0 remains analytic in the lower half k plane, and if

$$\int_0^\infty dr\, U(r) e^{\mu r} < \infty,$$

$\varphi_0(k,r)$ is also analytic in the upper half plane for $\text{Im}\, k < \mu/2$.

For $\ell = 0$, the Jost function $\varphi_0(k) = \varphi_0(k,0)$ so that $\varphi_0(k)$ is analytic in the k plane except for the cut. Similar results have been obtained for $\ell > 0$. From (1-169) it is seen that $\rho^*_{-k^*}(a)$ satisfies the same equation as $\rho_k(a)$ so that

$$\varphi_0(k) = \omega_0^*(-k^*), \tag{1-175}$$

and

$$S(k) = \frac{\varphi_0(k)}{\varphi_0(k^*)} \ . \tag{1-176}$$

For real positive k, $S(k) = \exp(2i\delta_0(k))$ and equation (1-176) shows that in this interval $\varphi_0(k)$ must have the phase $\delta_0(k)$,

$$\varphi_0(k) = |\varphi_0(k)| e^{i\delta_0(k)}, \tag{1-177a}$$

and on the negative real axis, from (1-175)

$$\varphi_0(-k) = |\varphi_0(k)| e^{-i\delta_0(k)}. \tag{1-177b}$$

Bound states and resonances

As a function of k, $S(k)$ is analytic apart from cuts along the imaginary axis in the intervals $+ \mu/2 < \text{Im}\, k < \infty$ and $- \mu/2 > \text{Im}\, k > -\infty$, and with the exception of possible poles arising from the zeros of the Jost function $\varphi_0(-k)$. Let us first locate the position of the zeros of $\varphi_0(-k)$ in the upper half k plane. Suppose these occur at $k = k_i = \lambda_i + i\mu_i$ with $\mu_i > 0$, then near these points $f_0^R(k,r)$ will behave at large r (from 1-165) like

$$f_0^R(k,r) \sim \varphi_0(+k_i)e^{i\lambda_i r}e^{-\mu_i r}.$$

These solutions are normalizable, and must therefore corres-
pond to bound states, but as the eigenvalues of H are real
(H is Hermitian), it follows that k_i^2 must be real and $\lambda_i = 0$.
The zeros in the upper half plane of $\varphi_0(-k)$ then all occur on
the imaginary axis and correspond to bound states. These
zeros give rise to poles in $S(k)$ also on the imaginary axis in
the upper half k plane at $k_i = i\mu_i$ (see figure 1-5) with cor-
responding zeros in the lower half plane at $k_i = -i\mu_i$.

The zeros in the lower half plane of $\varphi_0(-k)$ can occur
at any point $k_i = \lambda_i - i\mu_i$ and, by (1-175), are symmetrically
placed about the imaginary axis. They give rise to poles in $S(k)$
in the lower half plane and zeros in the upper half plane, as
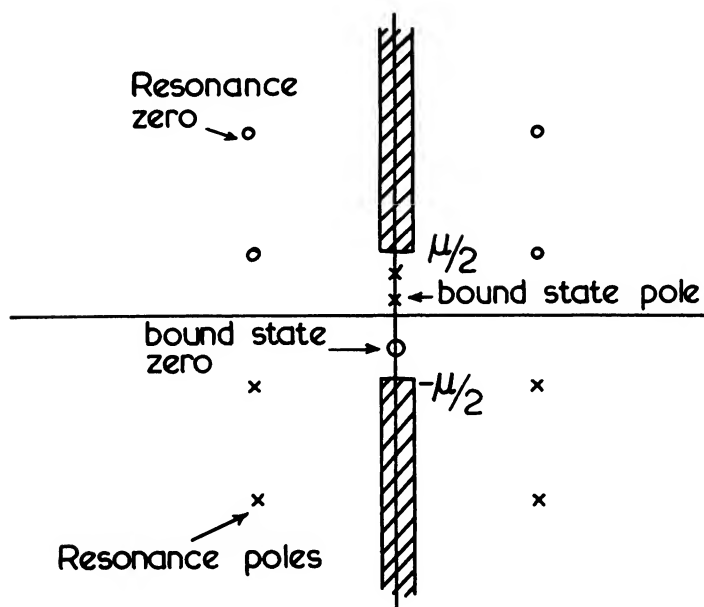shown in figure (1-4).

Figure 1-4   The structure of the S matrix element $S_0(k)$

Near one of the points $k = k_i - i\mu_i$, $\mu_i > 0$, $\varphi_0(-k)$ will have the form

$$\varphi_0(-k) = A(k - \lambda_i + i\mu_i)(k + \lambda_i + i\mu_i),$$

where A is a constant, showing the symmetrical disposition of the zeros about the imaginary axis. If k is real and the zero is near the real axis so that $\mu_i \ll \lambda_i$ we have, using (1-177b), that

$$\tan \delta_0(k) = \frac{2\mu_i k}{(k^2 - \lambda_i^2)} = \frac{\Gamma(E)}{2(E - E_R)}, \tag{1-178}$$

where $E = \hbar^2 k^2/2m$, $E_R = \hbar^2\lambda_i^2/2m$ and $\Gamma(E) = \hbar^2(2\mu_i k)/m$. The scattering amplitude $T_\ell = e^{i\delta_0} \sin \delta_0$ is then

$$T_\ell(E) = \left[\frac{-\Gamma(E)/2}{(E - E_R) + i\Gamma(E)/2} \right], \tag{1-179}$$

and the corresponding cross section is

$$\sigma_0(E) = \frac{\pi}{k^2} \frac{\Gamma^2(E)}{(E - E_R)^2 + \Gamma^2(E)/4}. \tag{1-180}$$

This is the famous Breit–Wigner formula for a narrow resonance. It is valid for values of E near E_R, if the width of the resonance $\Gamma(E)$ is small compared with the resonance position E_R. In general, the resonance will be superimposed on a slowly varying background. The asymptotic behaviour of the wave function $f_0^R(k,r)$ at the pole will be

$$f_0^R(k,r) \underset{r \to \infty}{\sim} \exp\{i\lambda r + \mu_i r\}\exp\left\{-i\left(E_R - \frac{\Gamma}{2}\right) t/\hbar\right\}, \tag{1-181}$$

where the time dependence appropriate to a state of energy $E = E_R - i\Gamma/2$ has been restored. It is seen that the wave function describes a state decaying in time, with a mean life time

$$\Upsilon = \frac{\hbar}{\Gamma}. \tag{1-182}$$

A scattering resonance can thus be interpreted as being due to the formation of a semi-bound state, provided Υ is long compared with the natural collision time. Such a state is often

known as a Siegert state.

As the poles in $S_0(k)$ occur in the lower half k plane, Γ is positive, which is consistent with the interpretation of the resonant state as a decaying state. The rate of change of the phase shift near the resonance is

$$\frac{\partial \delta_0(E)}{\partial E} = \frac{2}{\Gamma(E_R)} \cdot$$

This shows that, near a resonance, $\delta_0(E)$ is an increasing function of E, as was asserted on page 23.

An exceptional case occurs when $\varphi_0(-k)$ has a zero in the lower half plane on the imaginary axis. In this case the S-matrix has a pole at a negative real energy. This is not a bound state, however (this can be checked from looking at the asymptotic form of $f_0^R(k,r)$), but has been given the name 'anti-bound' state. The presence of such a state can have a pronounced influence on scattering at low energies if it is close enough to the physical threshold at $k^2 = 0$.

Levinson's theorem

The properties of the Jost function afford a simple proof of Levinson's theorem which was mentioned earlier (page 21). The integral I is formed where

$$I = \frac{1}{2\pi i} \int_C dk \left[\frac{d}{dk} \log \varphi_0(+k) \right]. \tag{1-183}$$

The contour is taken along the real axis and closed by an infinite semi-circle in the lower half plane. At each zero in $\varphi_0(+k)$ the integrand possesses a pole with unit residue, so that, by Cauchy's theorem

$$I = -n, \tag{1-184}$$

where n is the number of zeros in $\varphi_0(+k)$. Each zero in $\varphi_0(+k)$ in the lower half plane corresponds to a bound state, so that n is equal to the number of bound states of the system.

The contribution to I from the infinite semi-circle is zero, since $\omega_0(k) \to 1$ as $|k| \to \infty$. Then using (1-177a)

$$I = \frac{1}{2\pi i} \int_{-\infty}^{\infty} dk \left[\frac{d}{dk} \log\{ |\varphi_0(k)| e^{i\delta_0} \} \right].$$

Using the symmetry property (1-177b)

$$I = \frac{1}{2\pi i} \int_0^\infty dk \frac{d}{dk} \left[\log| e^{2i\delta_0(k)} | \right] = \frac{1}{\pi} \left(\delta_0(\infty) - \delta_0(0) \right).$$

(1-185)

Taking the phase shift at infinite energy to be zero, we have Levinson theorem that

$$\delta_0(0) = n\pi,$$ (1-186a)

where n is the number of bound states. An exceptional case that we have not allowed for occurs when there is a pole at zero energy[8] and in this case it can be shown that Levinson theorem holds in the form

$$\delta_0(0) = (n + \frac{1}{2})\pi.$$ (1-186b)

It should be noted that the extra term of $\pi/2$ occurs only for $\ell = 0$.

The effective range expansion

The scattering amplitude $T_\ell(k)$ is expressed in terms of the Jost function by

$$T_\ell(k) = \frac{\varphi_\ell(k) - \varphi_\ell(-k)}{2i\varphi_\ell(-k)}.$$ (1-187)

From the analytic properties of the Jost function, it can be shown, for potentials of the type (1-160), that $k^{2\ell+1} \text{Re} T_\ell^{-1}$ is analytic in E about the threshold at $E = 0$, within a circle of radius $(\mu^2 \hbar^2/8m)$, where μ is the lower limit in the integral 1-160. It follows that the expansion in k^2,

$$k^{2\ell+1} \text{Re}(T_\ell^{-1}) = k^{2\ell+1} \cot \delta_\ell = \frac{1}{a_s} + \frac{1}{2} r_0 k^2 + \ldots,$$

(1-188)

converges near zero energy. For $\ell = 0$ the parameter a_s is

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[8] A pole at zero energy, need not imply that a bound state of zero energy exists, but for some potentials such states can occur.

the scattering length (introduced on page 19), and r_0 is called the effective range. From Levinson's theorem, the phase shift $\delta_0 \to 0$ as $k \to 0$, if there are no bound states, and a_s is then positive. In this case a connection between the position of the bound state and the low energy scattering parameters can be made. The S-matrix for $\ell = 0$ can be written as

$$S_0(k) = \frac{\mathrm{Re}\,(T_0^{-1}) + i}{\mathrm{Re}\,(T_0^{-1}) - i} \quad .$$

The bound states occur at the poles of $S_0(k)$ on the positive imaginary axis at the points $k = i\lambda$, and at these points $\mathrm{Re}\,(T_0^{-1}) = i$. Using the effective range expansion for $(\mathrm{Re}\,T_0^{-1})$ we find

$$-\lambda = \frac{1}{a_s} - \frac{1}{2} r_0 \lambda^2 ,$$

which is the required relation between the bound state energy $E_B = -\hbar^2 \lambda^2 / 2m$ and the low energy scattering parameters a_s and r_0.

The result is easily generalized to all ℓ. In particular, at the bound states

$$\mathrm{Re}\,(T_\ell^{-1}) = i \quad \text{for any } \ell . \tag{1-189}$$

The effective range expansion converges rapidly even for strong interactions and is a great help in analysing experimental data at low energies. A generalization will be given later that is applicable in the case of inelastic many channel scattering.

1-8   CENTER OF MASS AND LABORATORY COORDINATES

To conclude this chapter, we shall show how the theory of potential scattering from a fixed center of force is related to the problem of two particles interacting via a potential that depends on their mutual separation. If the particles A and B are of mass m_A and m_B and possess momenta $\mathbf{q}_A$, $\mathbf{q}_B$ respectively, then the Hamiltonian in the momentum representation is

$$H = \frac{q_A^2}{2m_A} + \frac{q_B^2}{2m_B} + V. \tag{1-190}$$

Choosing a coordinate system in which the center of mass is at rest (called the center of mass system), it follows that

$$q_A = -q_B = q \tag{1-191}$$

and

$$H = \frac{1}{2\mu} q^2 + V, \tag{1-192}$$

where

$$\mu = \frac{m_A m_B}{m_A + m_B}.$$

The relative velocity of the particles is $q/\mu = (\dot{r}_A - \dot{r}_B)$ so that the canonically conjugate coordinate to p is the relative position vector of the two particles $r = r_A - r_B$. The Schrödinger equation is in the positive representation:

$$\left(-\frac{\hbar^2}{2\mu} \nabla^2 + V(r) \right) \Psi(r) = i\hbar \frac{\partial \Psi}{\partial t},$$

which is of the same form as the equation for scattering by a fixed center of force, with the reduced mass μ replacing m.

The probability that scattering has occurred cannot depend on the coordinate frame from which the event is viewed so that the total cross section,

$$\sigma = 2\pi \int_{-1}^{1} d \cos \theta |f_k(\theta)|^2,$$

is the same in all coordinate systems.

This fact may be used to connect the differential cross section in the center of mass system to that in the laboratory system in which the particle B is at rest. The invariance of σ requires that

$$\left. \frac{d\sigma}{d\Omega} \right|_{Lab} = \left. \frac{d\sigma}{d\Omega} \right|_{c.m.} \frac{d(\cos \theta')}{d(\cos \theta)}, \tag{1-193}$$

where θ is the scattering angle in the centre of mass system and θ' in the laboratory system.

The velocity of the center of mass in the laboratory system is $V = m_A U_A / m_A + m_B)$, where U_A is the incident

velocity of particle A. Suppose $\mathbf{V}_A$ is the final velocity of par-
ticle A in center of mass system and $\mathbf{V}'_A$ the same quality
in the laboratory system.

Then $\mathbf{V}_A$ and $\mathbf{V}_{A'}$ are related by

$$\mathbf{V}_A = \mathbf{V}'_A - \mathbf{V},$$

from which on taking components at right angles

$$V_A \sin \theta = V'_A \sin \theta',$$

$$V_A \cos \theta = V'_A \cos \theta' - V.$$

On dividing we find

$$\tan \theta' = \frac{\sin \theta}{\cos \theta + V/V_A}.$$

The magnitude of the velocity of A in the center of mass sys-
tem is the same before and after the collision. Before the
collision it is $(U_A - V)$ so that

$$V_A = U_A - V \frac{m_B}{m_A} V,$$

giving

$$\tan \theta' = \frac{m_B \sin \theta}{m_B \cos \theta + m_A}. \qquad (1-194)$$

Finally, on differentiating, the required relationship is

$$\frac{d}{d\Omega}\bigg|_{Lab} = \frac{d}{d\Omega}\bigg|_{c.m.} \frac{\left(m_A^2 + m_B^2 + 2m_A m_B \cos \theta\right)^{3/2}}{m_B^2 \left| m_B + m_A \cos \theta \right|}.$$

$$(1-195)$$

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SPECIAL METHODS IN
POTENTIAL SCATTERING

In Chapter 1 we saw how the solution to the problem of scattering by a potential could be obtained to any degree of accuracy, by solving the radial Schrödinger equation numerically to calculate the phase shifts. In addition, in the course of a discussion of the integral equations satisfied by the scattering amplitude, the Born approximation was introduced, which however has a limited range of usefulness. In this chapter some other methods are described for evaluating the phase shifts, or the complete scattering amplitude, approximately, that have particular advantages in various situations.

2-1   THE VARIATIONAL METHOD

We shall start by considering the integral

$$I[\bar{f}_{\ell}] = \int_{0}^{\infty} \bar{f}_{\ell}(r) \mathbf{L} \bar{f}_{\ell}(r) dr, \qquad (2-1)$$

where $\mathbf{L}$ is the operator

$$\mathbf{L} = \frac{-2m}{\hbar^2}(H_o + V - E) = \left(\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2} - U(r) + k^2\right), \qquad (2-2)$$

and $\bar{f}_{\ell}(r)$ is a function that satisfies boundary conditions of the same form as those satisfied by the real regular solution

of the radial Schrödinger equation. That is

$$\bar{f}_\ell(0) = 0; \quad \bar{f}_\ell(r) \sim \sin\left(kr - \frac{\ell\pi}{2}\right) + \bar{K}_\ell \cos\left(kr - \frac{\ell\pi}{2}\right). \quad (2\text{-}3)$$

If we set $\bar{f}_\ell = f_\ell$, where f_ℓ is the actual solution of the radial Schrödinger equation with these boundary conditions, then $\bar{K}_\ell \rightarrow K_\ell = \tan\delta_\ell$, and it is clear that $I = 0$, since $Lf_\ell(r) = 0$.

Now suppose that $\bar{f}_\ell = f_\ell + \Delta f_\ell$, where Δf_ℓ is a small quantity and

$$\Delta f_\ell(0) = 0, \quad \Delta f_\ell(r) \sim \Delta K_\ell \cos\left(kr - \frac{\ell\pi}{2}\right), \quad (2\text{-}4)$$

and $\Delta K_\ell = \bar{K}_\ell - K_\ell$. Then we have

$$I[\bar{f}_\ell] = \int_0^\infty f_\ell L \Delta f_\ell dr \dotplus \int_0^\infty \Delta f_\ell L \Delta f_\ell dr. \quad (2\text{-}5)$$

Writing

$$f_\ell L \Delta f_\ell = (f_\ell L \Delta f_\ell - \Delta f_\ell L f_\ell), \quad (2\text{-}6)$$

we find

$$I[\bar{f}_\ell] - I[\Delta f_\ell] = \int_0^\infty \left\{ f_\ell(r) \frac{d^2}{dr^2} \Delta f_\ell(r) - \Delta f_\ell(r) \frac{d^2}{dr^2} f_\ell(r) \right\} dr$$

$$= \underset{R\rightarrow\infty}{\text{Lim}} \left[f_\ell(r) \frac{d}{dr} \Delta f_\ell - \Delta f_\ell \frac{d}{dr} f_\ell \right]_0^R = -k\Delta K_\ell, \quad (2\text{-}7)$$

where in the last line the asymptotic forms of $\Delta f_\ell(r)$ and $f_\ell(r)$ have been employed.

This is an identity satisfied by all functions $\Delta f_\ell(r)$ of the required form. If we now take $\Delta f_\ell(r)$ to be a small quantity of the first order, for all values of r, then the functional $I[\Delta f_\ell]$ must be of the second order of smallness and can be neglected. If $\Delta I = I[\bar{f}_\ell] - I[f_\ell]$ is defined as the change in I under the variation $f_\ell \rightarrow f_\ell + \Delta_\ell$, it is seen that the quantity $(I + kK_\ell)$ is stationary under the variation, that is, to first order we have

$$\Delta(I + kK_\ell) = 0. \quad (2\text{-}8)$$

Suppose we now have a parameterized form for $f_\ell(r)$ denoted by

$f_\ell^t(r)$, that depends on parameters c_i, $i = 1$, --- n, and suppose that for certain values of the parameters f_ℓ^t can be made to coincide with the exact functions f_ℓ. Then a variation of

the type we are considering is achieved by letting $c_i \to c_i + \Delta c_i$ and $K_\ell \to K_\ell + \Delta K_\ell$. Expanding $\Delta(I + kK_\ell)$ by Taylor's theorem and retaining first order terms, we have

$$\Delta(I + kK_\ell) = \sum_{i=1}^{n} \frac{\partial I}{\partial c_i} \Delta c_i + \frac{\partial I}{\partial K_\ell} \Delta K_\ell + k\Delta K_\ell = 0. \qquad (2-9)$$

As the quantities Δc_i and ΔK_ℓ are independent, it follows that

$$\frac{\partial I}{\partial c_i} = 0, \qquad\qquad\qquad\qquad (2-10a)$$

and

$$\frac{\partial I}{\partial K_\ell} = -k. \qquad\qquad\qquad\qquad (2-10b)$$

These equations are sufficient to determine the parameters c_i and K_ℓ. A better value of K_ℓ, correct to the second order, can then be obtained by integration of (2-10b).

$$\tan \delta_\ell = K_\ell = K_\ell^t + \frac{1}{k} I[f_\ell^t], \qquad\qquad (2-11)$$

where K_ℓ^t is the value of K_ℓ obtained from equations (2-10). This procedure is due to Kohn (1948). An alternative procedure (Hulthén, 1944) is to determine K_ℓ by replacing equation (2-10b) by the equation

$$I(c_i, K_\ell) = 0. \qquad\qquad\qquad\qquad (2-12)$$

This again (by 2-8) ensures that $\Delta K_\ell = 0$ and provides a value of $K_\ell = \tan \delta_\ell$ correct up to terms of the second order.

　　　　Many variants of the variational method can be obtained by imposing different boundary conditions on the trial functions $f_\ell^t(r)$. For example, a variational principle for the determination of $\cot \delta_\ell$ arises if $f_\ell^t(r)$ is taken to have the asymptotic form

$$f_\ell^t(r) \sim \cot \delta_\ell \, \sin(kr - \ell\pi/2) + \cos(kr - \ell\pi/2). \quad (2\text{-}13)$$

All variational methods suffer from the severe disadvantage that if the difference between the trial function and the exact function cannot be made small for any values of the parameters, entirely erroneous results may be obtained. Also as the value of K_ℓ obtained is stationary, but not necessarily a minimum, there is no theoretical test as to which of two trial functions is superior.

An example is given in Table 2-1, where s wave phase shifts $(\ell = 0)$ are shown for scattering by the first order static potential between an electron and a hydrogen atom

$$U(r) = -2(1 + 1/r)e^{-2r}. \quad (2\text{-}14)$$

The results were obtained using the Kohn and Hulthén methods with the trial function (Massey and Moiseiwitsch, 1951)

$$f_0(r) = \sin(kr) + (c_1 + c_2 e^{-r})(1 - e^{-r})\cos(kr). \quad (2\text{-}15)$$

In this case the agreement with the exact phase shifts is good.

Table 2-1

Zero order phase shifts $(\ell = 0)$ for scattering by the potential $U(r) = -2(1 + \dfrac{1}{r})e^{-2r}$

Phase shifts in radians

k(a.u.)	Exact	Kohn and Hulthén	Schwinger
0.1	0.730	0.721	0.695
0.2	0.973	0.972	0.950
0.3	1.046	1.045	--
0.4	--	1.057	1.045
0.5	1.045	1.044	--
1.0	0.906	0.904	0.901

The Kohn–Hulthén variational method for the scattering amplitude

The variational method of Kohn and Hulthén is easily extended to the calculation of the complete scattering amplitude $f_{\mathbf{k}}(\theta)$. Two solutions of the Schrödinger equation (1-5) are defined with boundary conditions,

$$\Psi_1 \equiv \Psi_{\mathbf{k}}^+(\mathbf{r}) \sim e^{i\mathbf{k}\cdot\mathbf{r}} + r^{-1} e^{ikr} f_{\mathbf{k}}^+(\theta), \qquad (2\text{-}16a)$$

where θ is the polar angle of $\mathbf{r}$ with respect to $\mathbf{k}$ as axis, and

$$\Psi_2 \equiv \Psi_{\mathbf{k}'}^-(\mathbf{r}) \sim e^{i\mathbf{k}'\cdot\mathbf{r}} + r^{-1} e^{-ikr} f_{\mathbf{k}'}^-(\theta'), \qquad (2\text{-}16b)$$

where $|k| = |k'|$ and θ' is the polar angle of $\mathbf{r}$ with respect to $\mathbf{k}'$ as axis.

Functions $\bar\Psi_1, \bar\Psi_2$ are introduced which differ from Ψ_1, Ψ_2 by first order quantities,

$$\bar\Psi_i = \Psi_i + \Delta\Psi_i, \quad i = 1, 2, \qquad (2\text{-}17)$$

and the boundary conditions satisfied by $\Delta\Psi_i$ are taken to be

$$\Delta\Psi_1(\mathbf{r}) \sim \Delta f_{\mathbf{k}}^+(\theta) r^{-1} e^{ikr}, \qquad (2\text{-}18a)$$

$$\Delta\Psi_2(r) \sim \Delta f_{\mathbf{k}'}^-(\theta') r^{-1} e^{-ikr}. \qquad (2\text{-}18b)$$

The functional $I[\bar\Psi_1, \bar\Psi_2]$ is defined as

$$I[\bar\Psi_1, \bar\Psi_2] = (\bar\Psi_1, L\bar\Psi_2) \equiv \int \bar\Psi_2^* L\bar\Psi_1 \, d\mathbf{r}, \qquad (2\text{-}19)$$

where $L \equiv (\nabla^2 - U(r) + k^2)$, and remembering that $L\Psi_1 = L\Psi_2^* = 0$, it follows that

$$I[\bar\Psi_1, \bar\Psi_2] - I[\Delta\Psi_1, \Delta\Psi_2] = \int [\Psi_2^* \nabla^2(\Delta\Psi_1) - (\Delta\Psi_1)\nabla^2\Psi_2^*] d\mathbf{r}.$$

Let the integral on the right hand side of this equation be denoted by J. Then by using Green's theorem to transform the integral to a surface integral over a large sphere of radius R, we find

$$J = \underset{R \to \infty}{Lim} \ (R^2) \int d\Omega(\theta,\varphi) \left[\Psi_2^* \frac{\partial}{\partial r}(\Delta \Psi_1) - \Delta \Psi_1 \frac{\partial}{\partial r} \Psi_2^* \right]_{r=R}.$$

On using the asymptotic forms of Ψ_1 and Ψ_2, J reduces to

$$J = \underset{R \to \infty}{lim} \ (R^2) \int d\Omega(\theta,\varphi) \left[e^{-i\mathbf{k}' \cdot \mathbf{r}} \frac{\partial}{\partial r} \left(r^{-1} e^{ikr} \right) - \right.$$
$$\left. - r^{-1} e^{ikr} \frac{\partial}{\partial r} \left(e^{-i\mathbf{k}' \cdot \mathbf{r}} \right) \right]_{r=R} \Delta f_{\mathbf{k}}^+ (\theta)$$

$$= \underset{R \to \infty}{lim} \ (i) \int d\Omega(\theta,\varphi) e^{i(kR - \mathbf{k}' \cdot \mathbf{R})} (kR + \mathbf{k}' \cdot \mathbf{R}) \Delta f_{\mathbf{k}}^+ (\theta).$$

As $R \to \infty$ the integral must vanish unless $\mathbf{k}' \cdot \mathbf{R} = kR$, this requires that $\mathbf{R}$ is in the direction of $\mathbf{k}'$, and that $\cos \theta$ becomes equal to the angle of scattering for the transition $\mathbf{k} \to \mathbf{k}'$. As $\Delta f_{\mathbf{k}}^+$ is slowly varying function, it may be taken outside the integral, and setting $\mathbf{k}' \cdot \mathbf{R} = kR$ we find that

$$J = \underset{R \to \infty}{lim} \ (2\pi ikR) \Delta f_{\mathbf{k}}^+ (\theta) \int_{-1}^{1} dx \, e^{+ikR(1-x)} (1 + x),$$

where $x = \cos \theta'$ and θ' is the angle between $\mathbf{k}'$ and $\mathbf{R}$. The integral is elementary and becomes equal to $(2i/kR)$ for large R. The final result is then

$$I[\bar{\Psi}_1, \bar{\Psi}_2] - I[\Delta \Psi_1, \Delta \Psi_2] = -4\pi \Delta f_{\mathbf{k}}^+ (\theta). \tag{2-20}$$

If the $\Delta \Psi_i$ are of first order, $I(\Delta \Psi_1, \Delta \Psi_2)$ is of second order and may be neglected and we obtain the variation principle

$$\Delta I = I[\bar{\Psi}_1, \bar{\Psi}_2] - I[\Psi_1, \Psi_2] = -4\pi \Delta f_{\mathbf{k}}^+ (\theta). \tag{2-21}$$

It follows that if $\Delta I = 0$, the error in the scattering amplitude will be of second order (provided that the error in the wave function is of first order). The wave function may be parameterized with parameters c_i as in the variational methods for $\tan \delta_\ell$. Alternatively some specific functions can be used for $\bar{\Psi}_1$ and $\bar{\Psi}_2$. As an example, it is interesting to note that, by setting $\bar{\Psi}_1 = e^{i\mathbf{k} \cdot \mathbf{r}}$, $\bar{\Psi}_2 = e^{i\mathbf{k}' \cdot \mathbf{r}}$ the Born approximation is recovered. The validity of this procedure clearly requires that

$f_{\mathbf{k}}(\theta)$ is small, because with these trial functions $\Delta f_{\mathbf{k}} = f_{\mathbf{k}}$.

Schwinger's variational principle

A different variational principle is due to Schwinger. It can be applied both to the complete amplitude and to the partial wave amplitudes. Using the integral equations for $\Psi_{\mathbf{k}}^{+}$ and $\Psi_{\mathbf{k}}^{-}$, the scattering amplitude may be expressed in the following alternative forms

$$-\frac{(2\pi)\hbar^2}{m} f_{\mathbf{k}}(\theta) = T_{\mathbf{k}',\mathbf{k}}(\theta)$$

$$= \langle \varphi_{\mathbf{k}'} | V | \Psi_{\mathbf{k}}^{+} \rangle$$

$$= \langle \Psi_{\mathbf{k}'}^{-} | V - VG_0^{+}V | \Psi_{\mathbf{k}}^{+} \rangle$$

$$= \langle \Psi_{\mathbf{k}'}^{-} | V | \varphi_{\mathbf{k}} \rangle.$$

From these relations we have the identity

$$T_{\mathbf{k}',\mathbf{k}} = \frac{\langle \Psi_{\mathbf{k}'}^{-} | V | \varphi_{\mathbf{k}} \rangle \langle \varphi_{\mathbf{k}'} | V | \Psi_{\mathbf{k}}^{+} \rangle}{\langle \Psi_{\mathbf{k}'}^{-} | V - VG_0^{+}V | \Psi_{\mathbf{k}}^{+} \rangle} , \qquad (2-22)$$

and it is easily checked that this is stationary under the arbitrary variations

$$| \Psi_{\mathbf{k}}^{\pm} \rangle \rightarrow | \Psi_{\mathbf{k}}^{\pm} \rangle + \Delta | \Psi_{\mathbf{k}}^{\pm} \rangle.$$

For the particular case of s-wave scattering by a potential, using the standing wave Green's function (1-49), the Schwinger identity for $\tan \delta_0$ is

$$k \tan \delta_0 = \frac{\left[\int_0^{\infty} f_0(r) \sin(kr) U(r) dr \right]^2}{\int_0^{\infty} [f_0(r)]^2 U(r) dr - \int_0^{\infty} dr \int_0^{\infty} dr' \left[f_0(r) U(r) g_0^P(r,r') U(r') f_0(r') \right]} .$$

$$(2-23)$$

The big advantage of this form of variational principle is that it does not depend on the normalization of the trial functions. Taking advantage of this, Altshuler (1953) has used polynomial expressions as trial functions

$$f_o(r) = \sum_{n=1}^{N} c_n r^n , \qquad (2-24)$$

to compute $\tan \delta_o$ from the equations

$$\frac{\partial (\tan \delta_o)}{\partial c_n} = 0 \quad n = 1, \ldots N \qquad (2-25)$$

for the potential (2-14). His results for $N = 3$ are shown in Table 2-1. For the same number of parameters the results are not as accurate as those given by the Kohn and Hulthén methods, with this particular choice of trial function.

If plane waves are used as trial functions, the term in the denominator of (2-22), $\langle \varphi_{k'} | VG_o^+ V | \varphi_k \rangle$ is the second term of the Born expansion. The degree of difficulty of the calculation is then just that of calculating the second Born approximation, but the results obtained from the variational expression may be meaningful even if the Born series diverges.

Minimum principles

Although the variational methods we have discussed are of great value, in general the calculated phase shift is neither a maximum or a minimum value so that it is impossible to test which of two given trial functions is superior. This circumstance has led to an intensive search for methods that do provide a bound on the phase shifts.[1] For zero energy scattering Rosenberg and Spruch (1959) found a bound on the scattering length that could be applied in practice and which, most importantly, can be used in many particle scattering problems (provided that the target wave function is known).

The starting point of the discussion is the identity (2-7). We shall discuss the case $\ell = 0$. On dividing both sides by k^2 and taking the limit $k \to 0$, it is found that

$$I[\bar{u}] - I[\Delta u] = -\Delta a_s , \qquad (2-26a)$$

where

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[1] An excellent review of minimum principles with complete references to earlier work has been given by Spruch (1962).

$$\bar{u}(r) = \underset{k \to 0}{\ell t} \; k^{-1} f_0(r) \quad \text{and} \quad a_s = \underset{k \to 0}{\ell t} \; \delta_0/k. \qquad (2\text{-}26b)$$

Referring to the effective range expansion (1-189), it is seen that a_s is the scattering length. The boundary conditions satisfied by $u(r)$ are

$$u(0) = 0, \; u(r) \sim (a_s + r). \qquad (2\text{-}27)$$

The trial function $\bar{u}$ is equal to $(u + \Delta u)$ and

$$\bar{u}(0) = 0, \; \bar{u}(r) \sim (\bar{a}_s + r) \quad \text{and} \quad \bar{a}_s = a_s + \Delta a_s. \; (2\text{-}28)$$

With a given trial function $\bar{u}$, $I[\bar{u}]$ may be calculated, so that if we could bound or find the sign of $I[\Delta u]$, we would be able to bound the error in the scattering length a_s.

Suppose that the system has no bound state, then by the Raleigh-Ritz principle

$$\int \varphi H \varphi \, d\mathbf{r} = -\frac{\hbar^2}{2m} \int \varphi L_0 \varphi \, d\mathbf{r} \geq 0, \qquad (2\text{-}29)$$

where φ is a normalizable function and

$$L_0 = \left(\frac{d^2}{dr^2} - U(r) \right). \qquad (2\text{-}30)$$

The function $\Delta u(r)$ is not normalizable, but defining $I[\lambda, \Delta u]$ by

$$I[\lambda, \Delta u(r)] = \int_0^\infty \Delta u(r) e^{-\lambda r} L_0 \Delta u(r) e^{-\lambda r} dr, \qquad (2\text{-}31)$$

it follows that $I[\lambda, \Delta u] < 0$. A short calculation shows that

$$I[\lambda, \Delta u] - I[\Delta u] = \int_0^\infty \Delta u(r) \left(e^{-2\lambda r} - 1 \right) \left[\frac{d^2}{dr^2} \Delta u(r) - U(r) \Delta u(r) \right] dr +$$

$$+ \lambda^2 \int_0^\infty [\Delta u(r)]^2 e^{-2\lambda r} dr - 2\lambda \int_0^\infty \Delta u(r) \frac{d}{dr} [\Delta u(r)] e^{-2\lambda r} dr.$$

Each term on the right hand side vanishes as $\lambda \to 0$ so that as $I[\lambda, \Delta u] \leq 0$, it follows that $I[\Delta u] < 0$.

The required bound is then

$$\Delta a_s \leq -I[\bar{u}], \qquad (2\text{-}32a)$$

or

$$a_s \geq \bar{a}_s + I[\bar{u}].$$ (2-32b)

The problem is then to determine $\bar{u}$ to make the right hand side of (2.32b) as large as possible. In this case, if linear parameters are employed in the trial function this will be achieved by the Kohn variational method we described earlier.

This maximum principle for a_s can be extended to the case in which the potential supports bound states (Rosenberg et al., 1960). To do this, some results from the Raleigh-Ritz variational method for bound states are needed. Suppose φ_i are a normalizable set of independent functions, then the function

$$\Psi = \sum_i \lambda_i \varphi_i$$ (2-33)

where λ_i are constants, can be used as a trial function. Defining the integral I as

$$I = (\Psi, (H - E)\Psi) = \int \Psi^*(H - E)\Psi d\mathbf{r},$$ (2-34)

we have from the Raleigh-Ritz principle that

$$\frac{\partial I}{\partial \lambda_i} = 0, \quad i = 1, 2, \ldots.$$ (2-35)

These equations reduce to linear equations for the parameters λ_i of the form

$$\sum_j (H_{ij} - EN_{ij})\lambda_j = 0,$$ (2-36)

where

$$H_{ij} = (\varphi_i, H\varphi_j),$$ (2-37a)

$$N_{ij} = (\varphi_i, \varphi_j).$$ (2-37b)

The eigenvalues E can then be determined from the condition that these equations are compatible:

$$\det|\mathbf{H} - E\mathbf{N}| = 0,$$ (2-38)

where $\mathbf{H}$ and $\mathbf{N}$ are the matrices with elements H_{ij} and N_{ij}. The Hyllerass-Undheim theorem states that if n of the

roots of this equation E_1, E_2 ... E_n are negative, then there are at least n bound states of the system. If we order the roots so that $E_1 < E_2 < E_3$ ... then E_1 is an upper bound on the ground state energy, E_2 is an upper bound on the energy of the first excited state and so on. Consider a system for which it is known that one bound state exists and suppose φ_1 is a trial function which provides a variational estimate $E_1^{(0)}$ for the energy, then

$$E_1^{(0)} = H_{11}/N_{11} .$$

Now consider trial function $\Psi = \lambda_1 \varphi_1 + \lambda_2 \varphi_2$, where φ_2 is some other normalizable function. The product of the roots of equation (2.36) is given by $\det|\mathbf{H}|/\det|\mathbf{N}|$, so that

$$E_1 E_2 = \frac{H_{11} H_{22} - H_{12}^2}{N_{11} N_{22} - N_{12}^2} . \tag{2-39}$$

By the Schwartz inequality the denominator on the right hand side of (2.39) is positive, E_1 is negative and, as there is only one bound state, E_2 must be positive. It follows that

$$H_{22} \geq H_{12}^2/H_{11} , \quad (H_{11} < 0). \tag{2-40}$$

This result is applied by taking for φ_2 the function $\Delta u(r)$ which, as we saw earlier, may be treated as a normalizable function in this context. Using (2.40), a bound on $I[\Delta u]$ is found immediately

$$I[\Delta u] \geq \frac{\hbar^2}{2m} \frac{\left[\int_0^\infty \varphi_1(r) L(\Delta u) dr\right]^2}{H_{11}} . \tag{2-41}$$

As $L(\Delta u) = L(\bar{u}(r))$ the corresponding bound on the scattering length becomes

$$a_s \geq \bar{a}_s + I[\bar{u}] - \frac{\hbar^2}{2mH_{11}}\left[\int_0^\infty \varphi_1 L(\bar{u}) dr\right]^2 . \tag{2-42}$$

If the Kohn variation method is carried through for a trial function of the form $(\bar{u} + \lambda \varphi_1)$ where λ is a parameter, the value of a_s obtained is the same as the right hand side of (2-42). That is, the Kohn variational method provides a lower bound for a_s, if the trial function includes a term representing the bound state of the system. The result (2-42) is easily

generalized to case where several bound states exist,
by summing over a number of terms of the same form as the
last term in (2-42).

The comparison potential method

The method described for the determination of scatter-
ing lengths can be extended to scattering at non-zero energies.
It is necessary to subtract from the trial function those com-
ponents that correspond to eigenfunctions of the Hamiltonian
at all energies lower than the one considered. As the positive
eigenenergies form a continuum, the spectrum is first rendered
discrete by supposing the system to be placed in a large
spherical box of radius R where R is much greater than the
range of the potential. In practice this method, originally due
to Risberg (1956) and Percival (1957) has not proved as useful
as methods based on the monotonic variation of the phase shift
with potential described in Section 1-3, and they will not
be described here.

The method of comparison potentials (Blankenbecler
and Sugar, 1964) attempts to find a potential V_1 for which the
phase shift can be found exactly and for which $V_1 < V$, where V
is the potential in which we are interested. It then follows
from (1.62) that $\delta_\ell^1 > \delta_\ell$, where δ_ℓ^1 and δ_ℓ are the phase
shifts corresponding to the potentials V_1 and V respectively.
The method is of particular interest, because the potential V
can be a non-local (integral operator) potential like those that
arise in the theory of scattering by complex systems.

Suppose that V is positive, and consider the in-
equality

$$I = \left(\left(\Psi - \sum_{i=1}^{N} c_i \varphi_i\right), \ V\left(\Psi - \sum_{j=1}^{N} c_j \varphi_j\right)\right) \geq 0, \qquad (2-43)$$

where Ψ is a scattering wave function (such as $f_\ell(r)$) and the
φ_i form a discrete set of independent functions.

To minimize the left-hand side of the inequality with
respect to the parameters c_j, we require that

$$\frac{\partial I}{\partial c_i} = \sum_j c_j^* (\varphi_j, V\varphi_i) - (\Psi, V\varphi_i) = 0,$$

or

$$c_j^* = \sum_i (\Psi, V\varphi_i)(\mathbf{M}^{-1})_{ij},$$

where $\mathbf{M}$ is the matrix with elements $M_{ij} = (\varphi_i, V\varphi_j)$. Inserting these values of c_j, in (2-43), we find

$$(\Psi, V\Psi) - \sum_{ij} (\Psi, V\varphi_i)(\mathbf{M}^{-1})_{ij}(\varphi_j, V\Psi) \geq 0. \tag{2-44}$$

Since this is true for an arbitrary Ψ, we may write

$$V \geq V_S^N, \tag{2-45}$$

where V_S^N is defined as the sum of separable potentials

$$V_S^N = \sum_{i,j=1}^N |V\varphi_i) \, \mathbf{M}_{ij}^{-1} \, (\varphi_j V|. \tag{2-46}$$

By expanding the set of independent functions φ_i, a sequence of potential $V_S^N, V_S^{N+1}, \ldots$ can be defined and it can be shown in a similar way that

$$V_S^{N+1} > V_S^N, \tag{2-47}$$

By the monotonicity theorem, the corresponding phase shifts δ^N, are lower bounds on the exact phase shift δ, $\delta^N < \delta$, and as N increases δ^N approaches δ.

Separable potentials

The comparison potential is separable and in configuration space is of the form

$$K(r, r') = \sum_{i,j} \alpha_{ij} U_i(r) U_j(r'), \tag{2-48}$$

where the α_{ij} are a set of coefficients. The corresponding Schrödinger equation for the partial waves is

$$\left(\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2} + k^2\right) f_\ell(r) = \int_0^\infty K(r, r') f_\ell(r') dr'. \tag{2-49}$$

This equation has an exact solution which may be found as follows. Inserting the explicit form of the potential (2-48) into equation

(2-49), we find

$$\left[\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2} + k^2\right]f_\ell(r) = \sum_{ij}\alpha_{ij}U_i(r)N_j, \qquad (2-50)$$

where

$$N_j = \int_0^\infty U_j(r)f_\ell(r)dr. \qquad (2-51)$$

The solution of this equation can be obtained in terms of the standing wave Green's function $g_\ell^P(r,r')$. It is

$$f_\ell(r) = s_\ell(kr) + \sum_{ij}\alpha_{ij}\int_0^\infty g_\ell^P(r,r')U_i(r')dr'N_j, \qquad (2-52)$$

and the phase shift is given by

$$\tan\delta_\ell = \frac{1}{k}\int_0^\infty s_\ell(kr')\sum_{ij}\alpha_{ij}U_i(r')dr'\cdot N_j. \qquad (2-53)$$

It remains to find N_j and this may be done by multiplying (2-52) by $U_n(r)$ and integrating. We find

$$N_n = \int_0^\infty U_n(r)s_\ell(kr)dr + \sum_{ij}\alpha_{ij}\int_0^\infty dr\int_0^\infty dr'U_n(r)g_\ell^P(r,r')U_i(r')N_j. \qquad (2-54)$$

This is a set of simultaneous linear equations for the N_j with the solution

$$N_j = \sum_n\left[\frac{1}{1-\mathbf{M}}\right]_{jn}\int_0^\infty U_n(r)s_\ell(kr)dr, \qquad (2-55)$$

where $\mathbf{M}$ is the matrix with elements

$$M_{jn} = \sum_i\alpha_{in}\int_0^\infty dr\int_0^\infty dr'U_j(r)g_\ell^P(r,r')U_n(r'). \qquad (2-56)$$

As an example, if the potential consists of the single term $K(r,r') = U(r)U(r')$, we have

$$\tan \delta_\ell = - \frac{k^{-1} \left[\int_0^\infty s_\ell(kr) U(r) dr \right]^2}{1 - \int_0^\infty dr \int_0^\infty dr' U(r) g_\ell^p(r,r') U(r')}. \qquad (2-57)$$

This is an explicit expression for $\tan \delta_\ell$ in terms of the potential and does not involve the wave function $f_\ell(r)$. The solutions also take a simple form in momentum space and this will be discussed in Chapter 4. The method of comparison potentials, in common with the other methods described in this chapter, is not important for the solution of the single particle potential problem, because numerical solutions of the radial Schrödinger equations are easily obtained, but as we shall show later, the methods of this chapter can be used in the many particle problem, for which no exact numerical solution is feasible.

2-2 THE SCHRÖDINGER EQUATION AND THE FREDHOLM METHOD

The Schrödinger equation for the radial wave function of order ℓ for a particle moving in a potential λV is

$$(H_\ell + \lambda V - E)|f_\ell\rangle = 0. \qquad (2-58)$$

The kinetic energy operator H_ℓ is, as usual,

$$H_\ell = -\frac{\hbar^2}{2m}\left(\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2}\right) \qquad (2-59)$$

and V is a central potential

$$V = V(r).$$

Following the discussion given in Section 1-6, we know that the wave function and the transition matrix elements can be expressed as

$$|f_\ell(E)\rangle = (1 + \lambda G^+ V)|\varphi_\ell(E)\rangle, \qquad (2-60a)$$

$$T_\ell = \langle\varphi_\ell(E)|\lambda V + \lambda^2 V G^+ V|\varphi_\ell(E)\rangle, \qquad (2-60b)$$

where $|\varphi_\ell(E)\rangle$ is the unperturbed eigenvector and G^+ is the

complete Green's operator

$$G^{\pm} = (E \pm i\epsilon - H_{\ell} - \lambda V)^{-1} . \tag{2-61}$$

In terms of the free particle Green's operator G_0, where

$$G_0^{\pm} = (E \pm i\epsilon - H_{\ell})^{-1} , \tag{2-62}$$

we find immediately that

$$G^+ = RG_0^+ , \tag{2-63a}$$

where the resolvent R is defined by

$$R = (1 - \lambda G_0^+ V)^{-1} . \tag{2-63b}$$

The solution of the scattering problem reduces to the inversion of the operator $(1 - \lambda G_0^+ V)$, for once this is known, T_{ℓ} can be constructed, since

$$T_{\ell} = \lambda \langle \varphi_{\ell}(E) | VR | \varphi_{\ell}(E) \rangle . \tag{2-64}$$

In an explicit representation, $(1 - \lambda G_0^+ V)$ is a matrix of infinite dimension. If $(1 - \lambda G_0^+ V)$ had been of finite dimensions, the inverse matrix R could be obtained at once as the solution of the simultaneous equations

$$R(1 - \lambda G_0^+ V) = 1 . \tag{2-65}$$

The solution is

$$R_{ij} = \frac{A_{ji}}{D}$$

where D is the determinant

$$D(E) = \det(1 - \lambda G_0^+ V) \tag{2-66}$$

and A_{ij} is the cofactor of $(1 - \lambda G_0^+ V)_{ij}$. Both $\mathbf{A}$ and D can be expressed as polynomials in the parameter λ

$$D = 1 + \sum_{n=1}^{N} (-1)^n \lambda^n a_n \tag{2-67}$$

$$\mathbf{A} = D\mathbf{1} + \sum_{n=0}^{N} (-1)^n \lambda^n \mathbf{b}_n .$$

The coefficients of the expansion can be expressed in terms of the matrix elements of the kernel $\mathbf{K}$, where $\mathbf{K} \equiv (G_0^+ V)$, as

$$a_1 = \sum_i K_{ii}, \quad a_2 = \sum_{ij} \frac{1}{2!} \begin{vmatrix} K_{ii} & K_{ij} \\ K_{ji} & K_{jj} \end{vmatrix},$$

$$(2\text{-}68)$$

$$a_3 = \sum_{ijk} \frac{1}{3!} \begin{vmatrix} K_{ii} & K_{ij} & K_{ik} \\ K_{ji} & K_{jj} & K_{jk} \\ K_{ki} & K_{kj} & K_{kk} \end{vmatrix}, \quad \cdots$$

and

$$(\mathbf{b}_1)_{ij} = K_{ij}, \quad (\mathbf{b}_2)_{ij} = \sum_k \begin{vmatrix} K_{ij} & K_{ik} \\ K_{kj} & K_{kk} \end{vmatrix},$$

$$(2\text{-}69)$$

$$(\mathbf{b}_3)_{ij} = \frac{1}{2!} \sum_{k,\ell} \begin{vmatrix} K_{ij} & K_{ik} & K_{i\ell} \\ K_{kj} & K_{kk} & K_{k\ell} \\ K_{\ell j} & K_{\ell k} & K_{\ell \ell} \end{vmatrix}, \quad \cdots \cdots$$

The successive terms can be calculated from the recurrence relations

$$\mathbf{b}_n = \frac{1}{n-1} \left[\mathbf{K} (T_r \mathbf{b}_{n-1}) - (n-1) \mathbf{K} \cdot \mathbf{b}_{n-1} \right], \quad n > 1.$$

and

$$a_n = \frac{1}{n}(Tr\, \mathbf{b}_n). \qquad (2\text{-}70)$$

For matrices of infinite dimension, the expansions become power series in λ, and these series define the solution. It is of course necessary for the series for $\mathbf{A}$ and D to converge and this can be shown to be the case, for all values of λ (Morse and Feshbach, 1953), provided that $Tr(\mathbf{K})$ exists.

In the position representation the kernel $K(r,r')$ has the explicit form

$$K(r,r') = \frac{2m}{\hbar^2} \langle r | \mathbf{K} | r' \rangle = -\frac{1}{k} s_\ell (kr_<) e^+ (kr_>) U(r'), \quad (2\text{-}71)$$

where $r_<, r_>$ are the greater and lesser of r and r' respectively, from which we have that

$$\text{Tr}(\mathbf{K}) = -\frac{1}{k} \int_0^\infty dr s_\ell (kr) e_\ell^+ (kr) U(r). \quad (2\text{-}72)$$

This integral converges provided that $U(r)$ is less singular than $1/r^2$ at the origin and vanishes faster than $1/r$ at infinity.

It will now be shown that the phase shift can be determined from the Fredholm determinant D, and further that $D(E + i\epsilon)$ is identical to the Jost function $\varphi_\ell(-k)$ introduced in Chapter 1. Before doing this two important properties of the determinant D will be demonstrated. Using the definition of G_o^+, we may write

$$D = \det(1 - \mathbf{K}) = \det\left(\frac{E - H_\ell - \lambda V}{E - H_\ell}\right). \quad (2\text{-}73)$$

We can now use the theorem that the determinant of a matrix $\mathbf{A}$ is equal to the product of the eigenvalues of $\mathbf{A}$. If the system is enclosed in a large box to make the eigenvalues of $(H_\ell + \lambda V)$ and H_ℓ discrete and the eigenvalues are E_n and E_n^o respectively, it follows that

$$D = \prod_n \left[\frac{E - E_n}{E - E_n^o}\right].$$

Taking logarithms of both sides of the equation $\log D$ is expressed as the sum

$$\log D = \sum_n \log\left(\frac{E - E_n}{E - E_n^o}\right),$$

which is equivalent to the relation

$$D = \exp \text{Tr}[\log(1 - \mathbf{K})]. \quad (2\text{-}74)$$

The expansion of this expression in powers of λ again repro-
duces the series (2.67). Now consider a determinant that
contains a projection operator $|a\rangle\langle a|$

$$D = \det(\mathbf{1} + |a\rangle\langle a|\mathbf{B}). \tag{2-75}$$

Then

$$\log D = \text{tr} \log\{\mathbf{1} + |a\rangle\langle a|\mathbf{B}\},$$

or

$$\log D = \text{Tr}\left[|a\rangle \frac{1}{\langle a|\mathbf{B}|a\rangle} \left\{\langle a|\mathbf{B}|a\rangle - \frac{1}{2}\langle a|\mathbf{B}|a\rangle^2 + \ldots\right\}\langle a|\mathbf{B}\right].$$

Since

$$\text{Tr}[|a\rangle\langle a|\mathbf{B}] = \langle a|\mathbf{B}|a\rangle$$

we have

$$\log D = \log[1 + \langle a|\mathbf{B}|a\rangle],$$

or

$$D = 1 + \langle a|\mathbf{B}|a\rangle. \tag{2-76}$$

The Jost function

To show the identity of the Jost function $\varphi_\ell(-k)$ and
$D(E + i\epsilon)$, an integral equation for $\varphi_\ell(-k)$ is required. For
simplicity consider the case of $\ell = 0$. It can easily be veri-
fied by substitution that

$$F_0(\pm k,r) = e^{\mp ikr} + \lambda \int_0^\infty dr' g(r,r') u(r') F_0(\pm k,r') \tag{2-77}$$

is a solution of the Schrödinger equation for the potential
$\lambda V(r)$, with the boundary conditions (1-162), where $g(r,r')$ is
defined[2] by

$$g(r,r') = -k^{-1}(\sin kr \cos kr' - \cos kr \sin kr'), \quad r < r'$$
$$\tag{2-78}$$
$$= 0 \qquad\qquad\qquad\qquad\qquad\qquad\quad r > r'.$$

From the definition (1-164), the Jost functions are

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[2] Note that $g(r,r') = g_0^+(r,r') + \dfrac{1}{k} e_0(kr) s_0(kr)$.

$$\varphi_0(\pm k) = \underset{r \to 0}{\ell t}\, e^{\pm ikr} F_0(\pm k, r)$$

$$(2\text{-}79)$$

$$= 1 + \frac{\lambda}{k} \int_0^\infty dr'\, \sin kr'\, u(r') F_0(\pm k, r').$$

If the iterative solution of (2.77) is used for F_0, the resulting series is term by term the same as the expansion of $D(E \mp i\epsilon)$ in powers of λ. The two functions are therefore the same.

A theorem of Poincaré states that if a parameter appears in a differential equation like the radial Schrödinger equation and if that parameter does not appear explicitly in the boundary conditions, then the solution of the equation is an entire function of the parameter. As the solutions $F_0(\pm k, r)$ are defined by boundary conditions which are independent of λ, it follows that $D(E)$ or $\varphi(\pm k)$ are entire functions of λ and that the power series expansion in λ converges for all values of λ.

$D(E)$ is considered as a function of $E = \hbar^2 k^2/2m$ rather than of k, and because of the double valued nature of the relation between E and k, $D(E)$ has a branch point at $E = 0$. We can take the branch cut along the real axis $0 < E < \infty$, in which case the upper half k plane will map into the whole E plane, and $\varphi(-k)$ for k real and positive may be identified with the boundary value of D just above the cut

$$\underset{\epsilon \to 0^+}{\ell t}\, D(E + i\epsilon) = \varphi(-k),$$

and in a similar way

$$\underset{\epsilon \to 0^+}{\ell t}\, D(E - i\epsilon) = \varphi(+k).$$

As the phase of $\varphi(\pm k)$ is $\pm \delta$, where δ is the phase shift, we have that

$$D(E \pm i\epsilon) = |D(E)| e^{\mp i\delta}, \qquad (2\text{-}80)$$

showing that a knowledge of D is sufficient to solve the scattering problem. As $D(E)$ is analytic in the entire E plane except for the cut along the real axis, a dispersion relation may be written for $D(E)$ by integrating $(D(E') - 1)/(E' - E)$ round the contour shown in figure 2-1.
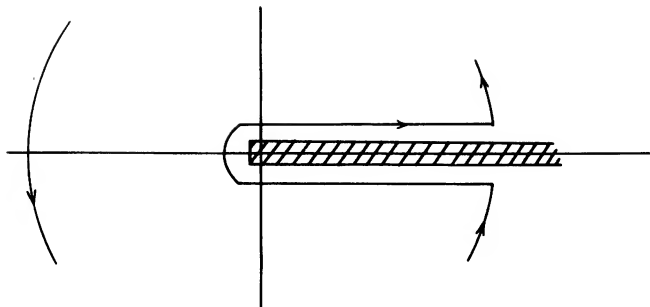
Figure 2-1   Contour for the integration leading to the dispersion relation for D(E),
Eq. (2-81).

Using Cauchy's theorem

$$D(E + i\epsilon) - 1 = \frac{1}{2\pi i} \int_C \frac{D(E') - 1}{E' - E - i\epsilon} dE'$$

$$= \frac{1}{\pi} \int_0^\infty \frac{\text{Im} D(E')}{E' - E - i\epsilon} dE' , \qquad (2-81)$$

where the fact that the discontinuity across the cut is $2i\text{Im}D$
has been used in the last line. This follows from the relation

$$D^*(E^*) = D(E).$$

These equations can be made the basis of a practical approxi-
mation (Baker, 1958; see also Nutt, 1964). For example, an
approximation to ImD could be obtained from the lowest terms
in the series (2-67), then ReD would be given by (2-81) and
the phase shift by (2-80). This procedure is closely related
to the "N/D" method frequently employed in high energy phys-
ics (Gasiorowicz, 1966).

Three dimensional and multi-channel scattering

The determinental method will not work, as it stands,
for the complete scattering amplitude because in this case

$$\text{Tr}[\mathbf{K}] = \int d\mathbf{r} \int d\mathbf{r}' \, G_0^+(\mathbf{r},\mathbf{r}') U(\mathbf{r}') \delta(\mathbf{r} - \mathbf{r}') \qquad (2-82)$$

does not exist. It is possible to extend the method to avoid
this difficulty, by subtracting the divergent parts of $\text{Tr}[\mathbf{K}]$.

For instance if $D(E)$ is defined as

$$D(E) = \exp \text{Tr}[\log(\mathbf{1} - \mathbf{K}) + \mathbf{K}], \qquad (2-83)$$

no divergent integrals appear in the expansion in powers of λ. Details may be found in the paper by Baker (1958).

The extension of the determinental theory to many channel scattering has been given by Blankenbecler (1963) and Blankenbecler and Sugar (1964).

2-3   SEMI-CLASSICAL SCATTERING FORMULAE

It is well known from the theory of optics, that when the wave-length of light is small compared with the distance over which the refractive index changes appreciably, then rays can be defined which follow the laws of geometrical optics. In the same way, if the wave-length (h/p) of a particle is sufficiently short compared with the distance in which the potential changes appreciably, it is possible to define particle trajectories which obey the laws of classical mechanics. There is an important approximation, that is useful at high energies, termed the semi-classical approximation which is intermediate in character between a full classical and a full quantum treatment.

If the potential is of range a, the short wave-length condition amounts to requiring that $ka \gg 1$.

When classical conditions hold, the angle of scattering must be well defined, that is the uncertainty $\Delta\theta$ in the angle of scattering must be small compared with θ. The uncertainty in the transverse momentum imparted to the scattered particle, Δp, is by Heisenberg's uncertainty principle, of the order (h/a),

$$\Delta p \sim h/a,$$

The corresponding uncertainty in the angle of scattering is

$$\Delta\theta = \frac{\Delta p}{p} \sim \left(\frac{1}{ka}\right),$$

and for classical conditions to apply, the angle of scattering θ must be greater than $(1/ka)$. If $\bar{V}$ is the average of the potential within the region $0 < r < a$, the momentum transfer in the transverse direction, hK, is of the order $(m\bar{V}/p)$, or in terms of $\bar{U}$ and k, $(h\bar{U}/2k)$. From this, it can be seen that the angle of scattering at small angles is approximately given by

$$\theta = \frac{K}{k} = \left(\frac{\overline{U}}{2k^2} \right).$$ (2-84)

From this result it follows that the inequality $\Delta\theta \ll \theta$ can be written as

$$\frac{a\overline{U}}{2k} \gg 1.$$

The Born approximation is also a high velocity approximation but it applies to angles of scattering within the cone $\theta < (\overline{U}/2k^2)$, whereas the classical scattering conditions apply when $\theta > (1/ka)$, and the two regions do not overlap.

Classical scattering cross-sections

Before exploring the classical and semi-classical limits of the Schrödinger equation, a brief discussion of classical scattering theory will be given. The starting point of the classical theory is the Lagrangian for a particle of mass m moving in the potential field $V(r)$. If the potential is central the motion takes place in a plane and if plane polar coordinates (r, φ) are introduced, with the center of force as origin, the Lagrangian is

$$\mathcal{L} = \frac{1}{2}m(\dot{r}^2 + r^2\dot{\varphi}^2) - V(r).$$

As φ is a cyclic coordinate, the angular momentum L where

$$L = \frac{\partial \mathcal{L}}{\partial \dot{\varphi}} = mr^2\dot{\varphi},$$ (2-85)

is a constant of the motion. The total energy E must also be conserved and

$$E = \frac{1}{2}m(\dot{r}^2 + r^2\dot{\varphi}^2) + V(r) = \frac{1}{2}m\dot{r}^2 + \frac{L^2}{2mr^2} + V(r)$$

is a constant. Solving the energy equation for $\dot{r} = dr/dt$, we find

$$\frac{dr}{dt} = \left[\frac{2}{m}(E - V(r)) - \frac{L^2}{m^2r^2} \right]^{\frac{1}{2}}$$ (2-86)

and integrating

$$t = \int dr \left[\frac{2}{m}(E - V(r)) - \frac{L^2}{m^2 r^2} \right]^{-\frac{1}{2}} + t_0, \qquad (2-87)$$

where t_0 is a constant of integration. By writing equation 2-85) in the form $dt = mr^2 d\varphi / L$, the orbit equation can be deduced from (2-87):

$$\varphi = \int_{r_0}^{r} dr \frac{L}{mr^2} \left[\frac{2}{m}(E - V(r)) - \frac{L^2}{m^2 r^2} \right]^{-\frac{1}{2}}$$

$$= -\int_{r_0}^{r} dr \frac{\partial}{\partial L} \left[2m(E - V(r)) - \frac{L^2}{r^2} \right]^{\frac{1}{2}}, \qquad (2-88)$$

where the constant of integration has been determined by requiring that $\varphi = 0$ at $r = r_0$, where r_0 is the distance of closest approach. This is determined by the equation $\dot{r} = 0$, and, by (2-86), r_0 is the root of the equation

$$2m(E - V(r)) = \frac{L^2}{r^2}. \qquad (2-89)$$

If a is the angle between the asymptotes of the orbit

$$\frac{a}{2} = \varphi(r = \infty) - \varphi(r = r_0) = -\int_{r_0}^{\infty} dr \frac{\partial}{\partial L} \left\{ 2m[E - V(r)] - \frac{L^2}{r^2} \right\}^{\frac{1}{2}}$$

$$(2-90)$$

and the angle of deflection Θ is defined as

$$\Theta = \pi - a.$$

If Θ lies in the interval $0 < \Theta < \pi$ and if Θ is a monotonic function of L, then Θ can be identified with the angle of scattering θ.

In general the deflection angle can take any value in the interval $-\infty < \Theta < \pi$, and the scattering angle which is defined to lie in the interval of $0 < \theta < \pi$ is

$$\theta = \pm\Theta + 2\pi m, \qquad (2-91)$$

where m is an integer or zero.

The differential cross-section is calculated by considering the scattering of a uniform beam of particles each of velocity v. If N particles cross unit area normal to the beam

per unit time, then the number per second with angular momen-
tum between L and L + dL is equal to the number per second
with impact parameters between b and b + db, where b = L/mv.
This number is

$$2\pi Nbdb = 2\pi NLdL/(m^2 v^2).$$

If the number of particles scattered per unit time between
angles θ and $\theta + d\theta$ is I, we see that

$$I = \frac{2\pi NL}{m^2 v^2} \left| \frac{dL}{d\theta} \right| d\theta, \tag{2-92}$$

where $L(\theta)$ is given by (2-90). The differential cross-section
$d\sigma/d\Omega$ is therefore (using $d\theta = -d(\cos\theta)/\sin\theta$)

$$\frac{d\sigma}{d\Omega} = \frac{+L}{m^2 v^2} \left| \frac{dL}{d\theta} \right| \frac{1}{\sin\theta}. \tag{2-93}$$

If there is more than one value of L satisfying equation (2-90)
for a given θ, then the classical cross section is the sum of
contributions from each branch of the function

$$\frac{d\sigma}{d\Omega} = + \sum_i \left[\frac{L_i}{m^2 v^2} \left| \frac{dL}{d\theta} \right|_i \frac{1}{\sin\theta} \right].$$

Coulomb scattering

As an example, if $V(r)$ is the coulomb potential
$Z_1 Z_2 e^2/r$ between two particles of charges $Z_1 e$ and $Z_2 e$, then
integration of (2-90) yields

$$\theta = \pi - 2 \cot^{-1}\left[\frac{Z_1 Z_2 e^2 \sqrt{m}}{L\sqrt{2E}} \right].$$

Inverting to obtain L, we find

$$L = \sqrt{\left(\frac{m}{2E}\right)} Z_1 Z_2 e^2 \cot(\theta/2),$$

and the differential cross-section is

$$\frac{d\sigma}{d\Omega} = \left[\frac{Z_1 Z_2 e^2}{4E} \right]^2 \frac{1}{(\sin\theta/2)^4}.$$

As $\theta \to 0$, the cross-section diverges. This is because some
scattering occurs however far the particle is from the center of

force, and large values of impact parameter b correspond to scattering through small angles. For this reason, the classical total cross section for Coulomb scattering, and for all potentials that do not vanish beyond a certain distance, is infinite.

The Eikonal approximation[3]

To investigate the classical limit of the Schrödinger equation the wave function $\Psi(\mathbf{r})$ can be written as

$$\Psi(\mathbf{r}) = e^{iS(\mathbf{r})/\hbar}. \tag{2-94}$$

On substituting into the time independent Schrödinger equation we find that

$$\frac{1}{2m}(-i\hbar\nabla^2 S + (\nabla S)^2) = E - V(r). \tag{2-95a}$$

The classical limit is obtained when $\nabla^2 S \ll (\nabla S)^2$ which is equivalent to taking the limit $\hbar \to 0$. In this limit, $S = S_0(\mathbf{r})$, where

$$\frac{1}{2m}(\nabla S_0)^2 = E - V(r), \tag{2-95b}$$

which will be recognized as the classical Hamilton-Jacobi equation, if $S_0(\mathbf{r})$ is identified with Hamilton's characteristic function. In optics this equation, which determines the rays, is called the eikonal equation. The integration of this equation determines the orbits, which are just those given by the more elementary theory and given by (2-88).

If $S_0(\mathbf{r})$ is substituted into (2-94) an approximation for the wave function is obtained that is termed the eikonal wavefunction. The use of this wave-function in the integral equation for the scattering amplitude (1-129), forms the basis of the eikonal approximation.

Under the conditions in which semi-classical methods are expected to be accurate, scattering is confined to small angles and the trajectory will be nearly a straight line parallel

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[3] For an extended review, with applications to nuclear physics, see Glauber (1959).

to the direction of incidence. Taking the center of force as
the origin of the coordinate system, with the Z-axis in the
direction of incidence, and defining $\hat{\mathbf{k}}$ as a unit vector para-
llel to the Z-axis, and $\mathbf{b}$ as a vector perpendicular to $\hat{\mathbf{k}}$ and
of length equal to the classical impact parameter, the orbit is
$\mathbf{r}(b)$, where

$$\mathbf{r} = \mathbf{b} + Z\hat{\mathbf{k}}$$

$$\mathbf{b} \cdot \hat{\mathbf{k}} = 0. \tag{2-96}$$

It is useful to note that $Z = vt$, where v is the velocity of the
particle and $t = 0$ is the time of closest approach. With the
approximation to the orbit, the eikonal equation (2-95) reduces
to

$$\frac{1}{2m}\left(\frac{\partial S_0(Z)}{\partial Z}\right)^2 = E - V(X,Y,Z), \tag{2-97}$$

with the solution

$$S_0(Z) = \int \left\{2m\left(E - V(\sqrt{b^2 + Z^2})\right)\right\}^{\frac{1}{2}} dZ + \text{constant}. \tag{2-98a}$$

The normalization required by the integral equation
(1-129) is that the wave function approaches a plane wave of
unit amplitude as $Z \to -\infty$. This condition is satisfied by the
approximate wave function provided

$$S_0(Z) \to \hbar kZ,$$

$$Z \to -\infty.$$

The approximate wave function does not have the correct
asymptotic form of a scattering wave function, in that it does
not describe out-going spherical waves at large r, but it
can represent the wave function over the region in which V is
large. Imposing the boundary condition, to determine the
integration constant it is found that

$$S_0(Z) = \hbar kZ + \int_{-\infty}^{Z} \left\{2m\left(E - V(\sqrt{b^2 + Z^2})\right)\right\}^{\frac{1}{2}} dZ. \tag{2-98b}$$

For large values of the momentum $\hbar k$, $S_0(Z)$ can be approxima-
ted as

$$S_0(Z) \simeq \hbar kZ - \frac{m}{\hbar k}\int_{-\infty}^{Z} V(\sqrt{b^2 + Z^2})\, dZ.$$

The scattering amplitude is then

$$f_{\mathbf{k}}(\theta) = -\frac{1}{4\pi}\int d\,re^{-i\mathbf{k}'\cdot\mathbf{r}}\,U(r)\exp\left\{i\left[\mathbf{k}\cdot\mathbf{r} - \frac{1}{2k}\int_{-\infty}^{Z}U(\sqrt{b^2+Z^2})dZ\right]\right\}$$

(2-99)

where r is given by (2-96) and $U(r) = 2mV(r)/\hbar^2$, as usual.

Introducing the momentum transfer $\mathbf{K} = \mathbf{k} - \mathbf{k}'$,
$|\mathbf{K}| = 2k\sin(\theta/2)$, we have that

$$\exp[i(\mathbf{k}\cdot\mathbf{r} - \mathbf{k}'\cdot\mathbf{r})] = \exp[i\mathbf{K}\cdot(\mathbf{b} + \hat{\mathbf{k}}Z)].$$

As $|\mathbf{k}'| = |\mathbf{k}|$, the momentum transfer, $\mathbf{K} = \mathbf{k} - \mathbf{k}'$, is nearly perpendicular to k for small angles of scattering θ,

$$\mathbf{K}\cdot\hat{\mathbf{k}} = k(1 - \cos\theta) \simeq \frac{1}{2}k\theta^2. \tag{2-100}$$

This is not an additional approximation as the eikonal approximation is only reliable for small angles, because of the assumption of straight line trajectories. The maximum value of Z of importance in the integration is ~a, where a is the range of the potential, so that the term $\exp(i\mathbf{K}\cdot\hat{\mathbf{k}}Z)$ may be replaced by 1 for angles such that $\theta^2 ka \ll 1$. Then

$$f_{\mathbf{k}}(\theta) = -\frac{1}{4\pi}\int_0^{2\pi}d\varphi\int_0^{\infty}bdb\int_{-\infty}^{\infty}dZe^{i\mathbf{K}\cdot\mathbf{b}}\,U(\sqrt{b^2+Z^2})\times$$

$$\times\exp\left\{-\frac{i}{2k}\int_{-\infty}^{Z}d\,ZU(\sqrt{b^2+Z^2}\right\}$$

$$= \frac{k}{2\pi i}\int_0^{2\pi}d\varphi\int_0^{\infty}bdbe^{i\mathbf{K}\cdot\mathbf{b}}\left[\exp\left\{-\frac{i}{2k}\int_{-\infty}^{\infty}U(\sqrt{b^2+Z^2})dZ\right\} - 1\right]$$

(2-101)

where φ is the azimuthal angle of **r**. The central potentials we are investigating do not depend on φ, and the φ integration is (Morse and Feshbach, p. 620),

$$\int_0^{2\pi}d\varphi\exp(iKb\cos\varphi) = 2\pi J_0(Kb),$$

We have finally,

$$f_k(\theta) = \frac{k}{i} \int_0^\infty J_0(Kb)[e^{i\chi(b)} - 1]b\,db, \qquad (2-102)$$

where the phase or eikonal $\chi(b)$ is defined by

$$\chi(b) = -\frac{1}{2k} \int_{-\infty}^\infty U(\sqrt{b^2 + Z^2})dZ. \qquad (2-103)$$

The eikonal approximation has several important properties.
For potentials of range a, $\chi(b)$ becomes small when $b > a$, so
that $f_k(\theta)$ receives contributions only from the range $0 < b < a$,
which is what would be expected classically. Calculation
(Glauber, 1959) shows that the optical theorem is satisfied by
$f_k(\theta)$, implying conservation of probability. This is in con-
trast to the Born approximation, for which the scattering ampli-
tude is real and which therefore can never satisfy the optical
theorem. The total cross-section is (using $J_0(0) = 1$),

$$\sigma(\text{tot}) = \frac{4\pi}{k}\text{Im}f_k(0) = -4\pi \int_0^\infty b\,db\,\text{Re}[e^{i\chi(b)} - 1]. \quad (2-104)$$

Impact parameter representations

It has been shown that the expression (2-102) is an
exact representation of the scattering amplitude (the particular
expression (2-103) for the phase is an approximation) for all
energies and angles (Adachi and Kotani, 1965, 1966; Predazzi,
1966; Chadan, 1968). To show this, a quantity $F(b)$ is
defined by the relation

$$F(b) = 2\int_0^1 y\,dy J_0(2byk)f_k(\theta), \qquad (2-105)$$

where $y = \sin(\theta/2)$. Expanding $f_k(\theta)$ in the partial wave
series

$$f_k(\theta) = \sum_{\ell=0}^\infty (2\ell + 1)k^{-1}T_\ell(k)P_\ell(\cos\theta),$$

and using the relation (Morse and Feshbach, 1953)

$$2bk \int_0^1 yJ_0(2byk)P_\ell(\cos\theta)dy = J_{2\ell+1}(2bk), \qquad (2-106)$$

it is found that

$$F(b) = \frac{1}{bk^2} \sum_{\ell=0}^{\infty} (2\ell + 1)J_{2\ell+1}(2bk)T_\ell(k). \qquad (2-107)$$

This may be inverted using the orthogonality relation for Bessel functions

$$2(2\ell + 1) \int_0^{\infty} dx x^{-1} J_{2\ell+1}(x)J_{2\ell'+1}(x) = \delta_{\ell\ell'}, \qquad (2-108)$$

to give

$$T_\ell(k) = 2k^2 \int_0^{\infty} db F(b)J_{2\ell+1}(2bk). \qquad (2-109)$$

Summing the partial wave amplitudes, the inverse relation to (2-105) is found to be

$$f_k(\theta) = 2k^2 \int_0^{\infty} bdb J_0(2bky)F(b), \qquad (2-110)$$

where we have used

$$\sum_\ell (2\ell + 1)J_{2\ell+1}(2bk)P_\ell(\cos\theta) = kbJ_0(2kby). \qquad (2-111)$$

The representation of $F(b)$ by the phase $\chi(b)$ is then quite general

$$F(b) = \frac{1}{2ik}\left[e^{i\chi(b)} - 1 \right], \qquad (2-112)$$

and it ensures that the unitarity condition $|T_\ell| \leq 1$ is satisfied. When semi-classical conditions apply, the phase $\chi(b)$ may be related to the phase shifts δ_ℓ. For small θ and large ℓ:

$$P_\ell(\cos\theta) \simeq J_0(2\ell y), \qquad (2-113)$$

and if the sum over ℓ in the partial wave series is approximated by an integration, we find

$$f_k(\theta) \simeq \frac{1}{ik} \int_0^{\infty} \ell d\ell J_0(2\ell y)\left(e^{2i\delta_\ell} - 1 \right). \qquad (2-114)$$

Comparing with (2-102), it is seen that

$$2\delta_\ell = \chi(b),\tag{2-115}$$

where b and ℓ are related by $\ell = kb$.

The eikonal approximation is equally valid for real and absorptive potentials. In the latter case, χ becomes complex and

$$\mathrm{Re}\chi = 2\delta_\ell,$$

$$\exp[-\mathrm{Im}\chi] = \eta_\ell.$$

Scattering by a black sphere

An example is given by scattering from a perfectly absorbing 'black' sphere of radius a. For $\ell < ka$, we may put $\eta_\ell = 0$ which corresponds to complete absorption, while for $\ell > ka$, the partial wave scattering amplitude vanishes, so that

$$f_{\mathbf{k}}(\theta) = \frac{1}{2ik}\int_0^{ka} \ell\, d\ell\, J_0(2\ell y)$$

$$= ia\frac{J_1(2kay)}{2y}.\tag{2-116}$$

The cross section has a typical diffraction shape, peaked in the forward direction, with subsidiary decreasing peaks as θ increases. The total cross section is

$$\sigma_{tot} = \frac{4\pi}{k}\,\mathrm{Im}f_{\mathbf{k}}(0) = 2\pi a^2.$$

As the sphere is completely absorbing, each partial inelastic cross section $\sigma_\ell(in)$ takes on its maximum value of $\pi(2\ell+1)/k^2$ and the complete inelastic cross section is

$$\sigma(in) = \sum_{\ell=0}^{ka} \frac{\pi(2\ell+1)}{k^2} = \pi a^2.$$

As pointed out earlier (Section 1-5), when the cross section for inelastic scattering in a particular partial wave takes on its maximum value, then the elastic scattering cross section

σ_ℓ (eℓ) has an equal value. It follows that

$$\sigma(e\ell) = \pi a^2.$$

in conformity with (1-98a) and (1-98b). The elastic cross section can also be found by integrating $|f_k(\theta)|^2$ given by (2-116).

The Jeffreys or W.K.B. method

A more elaborate approximation can be obtained if the phase shifts δ_ℓ are computed semi-classically from the radial Schrödinger equation (Jeffreys, 1923; Wentzel, 1926; Brillouin, 1926; Kramers, 1926). This has the advantage that the angular momentum eigenfunctions are treated exactly. The computed phase shifts may then be used in the partial wave series or, more conveniently, as under the conditions for which the semi-classical method is valid there may be a very large number of important partial waves, the phase shifts may be used in an integral expression such as (2-114).

The treatment of the Jeffreys method that we shall follow is based on the work of Langer (1937; see also Morse and Feshbach, 1953, p. 1092). It is easiest to start from the one dimensional Schrödinger equation

$$\left[\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) - E\right]\Psi(x) = 0, \tag{2-117}$$

where $\Psi(x)$ is defined in the interval $-\infty < x < \infty$. A change of variable will be made later to transform the radial Schrödinger equation into this form at a later stage.

As in the eikonal method, we look for a solution in the form

$$\Psi(x) = e^{iS(x)/\hbar}. \tag{2-118}$$

Substitution into the Schrödinger equation shows that $S(x)$ satisfies

$$-i\hbar\frac{d^2S}{dx^2} + \left(\frac{dS}{dx}\right)^2 = F(x), \tag{2-119}$$

where $F(x) = 2m[E - V(x)]$. Expanding $S(x)$ in powers of $\hbar$ gives us

$$S = S_0(x) + \hbar S_1(x) + \hbar^2 S_2(x) + \dots ,$$

and substituting into equation (2-119) and equating the

coefficients of each power of $\hbar$, we find

$$\left(\frac{dS_0}{dx}\right)^2 = F(x) \tag{2-120a}$$

$$- i\frac{d^2 S_0}{dx^2} + 2\frac{dS_0}{dx}\frac{dS_1}{dx} = 0 \tag{2-120b}$$

$$- i\frac{d^2 S_1}{dx^2} + \left(\frac{dS_1}{dx}\right)^2 + 2\frac{dS_0}{dx}\frac{dS_2}{dx} = 0 \tag{2-120c}$$

. . . .

On integrating (2-120a), $S_0(x)$ is immediately found to be

$$S_0(x) = \pm \int F^{\frac{1}{2}}(x)dx. \tag{2-121}$$

The next term $S_1(x)$ is found by using S_0 in equation (2-120b) and integrating,

$$S_1(x) = i\log|F(x)|^{+\frac{1}{4}}. \tag{2-122}$$

The equation for dS_2/dx, (2-120c), depends on the value of

$$\frac{dS_1}{dx} = \frac{i}{4F(x)}\frac{d|F(x)|}{dx}$$

$$= \frac{-im}{2F(x)}\frac{\partial V(x)}{\partial x}. \tag{1-123}$$

The classical limit is applicable when the potential varies slowly compared with the variation of $S(x)$. This requires that $\left|\frac{1}{F(x)}\frac{\partial V}{\partial x}\right|$ is small, $\ll 1$. In these circumstances S_2 and higher terms in the series for S can be neglected, as these are of the order $\left(\frac{1}{F(x)}\frac{\partial V}{\partial x}\right)^2$.

Provided this condition is satisfied, the most general solution for the case where $E > V(x)$, $F(x)$ positive, is

$$\Psi_+(x) = |F(x)|^{-\frac{1}{4}}\left\{A\exp\left[\frac{i}{\hbar}\int dx' F(x')^{\frac{1}{2}}\right] + B\exp\left[-\frac{i}{\hbar}\int dx' F(x')^{\frac{1}{2}}\right]\right\}, \tag{2-124}$$

and that for $E < V(x)$, $F(x)$ negative, is

$$\Psi_-(x) = |F(x)|^{-\frac{1}{4}}\left\{C \exp\frac{1}{\hbar}\int dx'|F(x')|^{\frac{1}{2}} + D \exp-\frac{1}{\hbar}\int dx'|F(x')|^{\frac{1}{2}}\right\},$$

$$(2-125)$$

where A, B, C and D are arbitrary constants.

The case that will be of interest to us is that in which $F(x)$ has a zero at $x = x_0$, say, where $F(x) < 0$ for $x < x_0$, $F(x) > 0$ for $x > x_0$. Under these circumstances, for large negative x, the solution satisfying the boundary condition $\Psi(x) \to 0$ as $x \to -\infty$, is

$$\Psi_-(x) = |F(x)|^{-\frac{1}{4}} D \exp\left[-\int_x^{x_0} \frac{1}{\hbar}dx|F(x)|^{\frac{1}{2}}\right]. \qquad (2-126)$$

The problem is then to determine the corresponding solution in the region $x \approx x_0$. This is not a simple problem as in the vicinity of x_0, which is the classical turning point, the solution breaks down completely, because the condition that $\left(\frac{1}{F}\frac{\partial V}{\partial x}\right)$ is small is violated.

<u>Connecting formulae</u>

To join the solutions to the left and right of the turning point, a solution is required that is valid in the region where $|(x - x_0)|$ is small. This suggests that $F(x)$ is expanded about the zero as

$$F(x) \approx A^2 (x - x_0).$$

The Schrödinger equation is then for small $|x - x_0|$,

$$\left[\frac{d^2}{dx^2} + \frac{A^2}{\hbar^2}(x - x_0)\right]\Psi(x) = 0.$$

This equation has a solution which is a linear combination of the Bessel functions

$$\sqrt{(x - x_0)}\, J_{\pm 1/3}\left[\frac{2}{3}\frac{A}{\hbar}(x - x_0)^{3/2}\right].$$

The solutions $\Psi_{\pm}(x)$ depend on the integral

$$W(x) = \frac{1}{\hbar}\int_{x_0}^{x} F^{\frac{1}{2}}(x)dx. \qquad (2-127)$$

When $|x - x_0|$ is small, $W(x)$ reduces to the argument of the Bessel function, that is to $2/3 \, A/\hbar(x - x_0)^{3/2}$. It follows that the function

$$P = \frac{W}{|F(x)|} \left[E J_{1/3}(W) + F J_{-1/3}(W) \right], \qquad (2-128)$$

is an approximation for $\Psi(x)$ near $x = x_0$. From the asymptotic form of the Bessel functions:—

$$J_\nu(x) \sim \sqrt{\frac{2}{\pi x}} \, \cos\left(x - \frac{\pi \nu}{2} - \frac{\pi}{4}\right), \qquad (2-129)$$

it is seen that $P(x)$ becomes a linear combination of the solutions Ψ_- and Ψ_+ for large $|x|$. The error in P (Morse and Feshbach, 1953) is of the order $\partial^2 V/\partial x^2$ which is small when the semi-classical approximation is valid.

It is now straightforward to verify that the particular solution $\Psi_+(x)$ for $x \gg x_0$ that joins the solution vanishing at $x = -\infty$, is

$$\Psi_+(x) = \text{constant} \cdot F(x)^{-\frac{1}{4}} \cos\left[\int_{x_0}^{x} \frac{1}{\hbar} |F(x)|^{\frac{1}{2}} dx - \frac{\pi}{4}\right]. \quad (2-130)$$

The radial Schrödinger equation

The radial Schrödinger equation,

$$\left[\frac{d^2}{dr^2} - \frac{\ell(\ell + 1)}{r^2} + k^2 - U(r)\right] f_\ell(r) = 0,$$

cannot be treated in the same way as the one-dimensional equation because of the singularity at $r = 0$. It can, however, be brought into the form of the one dimensional equation by the substitutions

$$x = \log r; \quad \Psi = r^{-\frac{1}{2}} f_\ell(r), \qquad (2-131)$$

giving

$$\frac{d^2 \Psi}{dx^2} + e^{2x}\left[k^2 - U(e^x) - e^{-2x}(\ell + \tfrac{1}{2})^2\right]\Psi = 0. \qquad (2-132)$$

Setting

$$F(x) = e^{2x}\left[k^2 - U(e^x) - e^{-2x}(\ell + \frac{1}{2})^2\right]$$ the required solu-

tion is given by equation (2-130) since the boundary condition
$f_\ell(0) = 0$ corresponds to $\Psi(x) \to 0$ at $x \to -\infty$.

Returning to the original variable r, the radial wave
function is

$$f_\ell(r) = CF(r)^{-\frac{1}{4}} \cos\left[\int_{r_o}^{r} dr' F^{\frac{1}{2}}(r') - \frac{\pi}{4}\right], \qquad (2-133)$$

where $F(r) = k^2 - U(r) - (\ell + 1/2)^2/r^2$. For large r, $F(r) \to k^2$
so that

$$\int_{r_o}^{r} F^{\frac{1}{2}}(r')dr' \to \int_{r_o}^{\infty}\left[F^{\frac{1}{2}}(r') - k\right]dr' + k(r - r_o), \qquad (2-134)$$

and comparing with the form $f_\ell(r) \sim \sin\left(kr - \frac{\ell\pi}{2} + \delta_\ell\right)$, the
phase shift δ_ℓ may be identified as

$$\delta_\ell = \int_{r_o}^{\infty}\left[F^{\frac{1}{2}}(r') - k\right]dr' + \left(\ell + \frac{1}{2}\right)\frac{\pi}{2} - kr_o. \qquad (2-135)$$

This expression is accurate for large values of ℓ, which can
be treated as a continuous variable, and δ_ℓ can be used in
equation (2-114). For large ℓ, the angular momentum L is

$$L = \hbar\sqrt{\ell(\ell + 1)} \simeq \hbar\left(\ell + \frac{1}{2}\right), \qquad (2-136)$$

and in terms of L, δ_ℓ can be written as

$$\delta_\ell = \frac{1}{\hbar}\int_{r_o}^{\infty}\left\{\left[2m(E - V(r)) - \frac{L^2}{r^2}\right]^{\frac{1}{2}} - k\hbar\right\}dr + \frac{L\pi}{2\hbar} - kr_o.$$

$$(2-137)$$

Differentiating with respect to L

$$\hbar\frac{\partial\delta_\ell}{\partial L} = \frac{\pi}{2} + \int_{r_o}^{\infty}\frac{\partial}{\partial L}\left\{2m(E - V) - \frac{L^2}{r^2}\right\}^{\frac{1}{2}}dr, \qquad (2-138)$$

and comparing with (2-90) it is seen that twice the right hand side is identical with the classical deflection angle Θ

$$h\frac{\partial \delta_\ell}{\partial L} = \frac{1}{2}\Theta, \qquad L = \left(\ell + \frac{1}{2}\right)h. \tag{2-139}$$

The scattering amplitude

To determine the scattering amplitude, the approximation (2-137) for the phase shifts may be used in equation (2.114). For our present purpose, it is slightly more convenient to write the large ℓ approximation for $P_\ell(\cos(\theta))$ in the form

$$P_\ell(\cos(\theta)) \sim \left[\frac{1}{2}\left(\ell + \frac{1}{2}\right)\pi \sin \theta\right]^{-\frac{1}{2}} \sin\left[\left(\ell + \frac{1}{2}\right)\theta + \frac{\pi}{4}\right], \tag{2-140}$$

instead of in terms of $J_0(2\ell y)$. This approximation is valid for $\ell \gtrsim 1/\sin \theta$. As large ℓ values (of the order (ka)) are the most important, it follows that the approximation will be good for angles down to $\theta \simeq 1/ka$, which is of course small since $ka \gg 1$.

In the partial wave series for the scattering amplitude $f_k(\theta)$, the term not involving the phase shift can be summed, as

$$\frac{1}{2}\sum_{\ell=0}^{\infty}(2\ell + 1)P_\ell(\cos \theta)P_\ell(1) = \delta(\cos \theta - 1), \tag{2-141}$$

by the closure relation for the Legendre polynomials. This part of $f_k(\theta)$ contributes only in the forward direction and may therefore be omitted, as it is required that $\theta \gtrsim 1/ka$. The remainder of the scattering amplitude is given by

$$f_k(\theta) = -\frac{1}{2k}\left[\frac{\pi \sin \theta}{2}\right]^{-\frac{1}{2}}\int_0^\infty\left(\ell + \frac{1}{2}\right)^{\frac{1}{2}}\left[e^{i\varphi_+} - e^{i\varphi_-}\right]d\ell, \tag{2-142a}$$

where the asymptotic form (2-140) of the Legendre polynomials has been employed and

$$\varphi_\pm = 2\delta_\ell \pm \left(\ell + \frac{1}{2}\right)\theta \pm \frac{\pi}{4}. \tag{2-142b}$$

The integral can be evaluated by the method of stationary phase. Because of the oscillating nature of the integrand the only non-zero contributions to the integral will arise from points $\ell = \ell_i$, where

$$\frac{d\varphi^{\pm}}{d\ell} = 0. \qquad (2\text{-}143)$$

If $\ell = \ell_o$ is such a point,[4] then close to ℓ_o

$$\varphi_{\pm}(\ell) = \varphi_{\pm}(\ell_o) + \frac{1}{2}\varphi_{\pm}''(\ell_o)(\ell - \ell_o)^2. \qquad (2\text{-}144)$$

The condition $d\varphi^{\pm}/d\ell = 0$ reduces to (using 2-142b, 2-139)

$$\theta = \pm\Theta(\ell_o), \qquad (2\text{-}145)$$

$$\varphi_{\pm}''(\ell_o) = \frac{d\Theta}{d\ell}\bigg|_{\ell=\ell_o}. \qquad (2\text{-}146)$$

The scattering angle θ must be positive, and this determines the sign to be used in (2-145). The deflection angle Θ is positive for a repulsion and negative for an attraction. Extending the integral from $-\infty$ to $+\infty$, we have

$$f_k(\theta) = -\frac{1}{2k}\left[\frac{\pi \sin\theta}{2}\right]^{-\frac{1}{2}}\left(\ell_o + \frac{1}{2}\right)^{\frac{1}{2}}\int_{-\infty}^{\infty}d\ell\, e^{i(\ell-\ell_o)^2\varphi''/2}\, e^{i\varphi_{\pm}(\ell_o)} \qquad (2\text{-}147)$$

$$= -\frac{1}{2k}\left[\frac{\sin\theta}{2}\right]^{-\frac{1}{2}}\left[\frac{2}{i\varphi_{\pm}''(\ell_o)}\right]^{\frac{1}{2}}e^{i\varphi_{\pm}(\ell_o)}\left(\ell_o + \frac{1}{2}\right)^{\frac{1}{2}}$$

In terms of $L = (\ell_o + 1/2)\hbar$, where ℓ_o is found from (2-145)

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[4] This condition can be expressed alternatively in terms of the impact parameter b and the phase $\chi(b)$. Since $\chi(b) = 2\delta_{\ell}$, we have

$$\varphi_{\pm}(b) = \chi(b) \pm mvb\theta \pm \frac{\pi}{4}$$

and the stationary point $b = b_o$ is found from the equation

$$\frac{d\varphi_{\pm}(b)}{db} = 0.$$

$$\frac{d\sigma}{d\Omega} = |f_{\mathbf{k}}(\theta)|^2 = L\left|\frac{dL}{d\theta}\right|/(m^2 v^2 \sin\theta), \tag{2-148}$$

which is the classical result (2-93) and it is valid at a given angle θ, if ℓ_0 found from (2-145) is large.[5]

In evaluating the integral, it was assumed that only one stationary point existed. If this is so, the classical angular distribution is obtained, but if this is not so, very different distributions may be obtained, even though the semi-classical conditions are well satisfied. The exceptional cases have been examined by Ford and Wheeler (1959), and we shall discuss their work briefly.

Interference effects

As in classical scattering, discussed on page 78, more than one value of the angular momentum may give rise to a given angle of scattering; in that case equation (2-143) or (2-145) is satisfied when ℓ is equal to ℓ_0, ℓ_1, $\ell_2 \dots$. Each term in the scattering amplitude will then have the phase $\varphi_{\pm}(\ell_i) = \beta_i$ and the 'semi-classical' differential cross section will be

$$\frac{d\sigma}{d\Omega} = \left|\sum_i \left|\frac{d\sigma}{d\Omega}\right|_i^{\frac{1}{2}} e^{i\beta_i}\right|^2, \tag{2-149}$$

where $(d\sigma/d\Omega)_i$ is the classical cross section arising from the ith branch of the deflection function. A situation in which this might occur is shown in figure 2-2, where $\Theta(\ell)$ is plotted against ℓ.

The line $\theta = \Theta(\ell)$ intercepts the curve twice at the points $\ell = \ell_0$ and $\ell = \ell_1$. As θ changes, the differential cross section will oscillate between the values

$$\left(\frac{d\sigma}{d\Omega}\right)_{\pm} = \left|\left(\frac{d\sigma}{d\Omega}\right)_0^{\frac{1}{2}} \pm \left(\frac{d\sigma}{d\Omega}\right)_1^{\frac{1}{2}}\right|^2, \tag{2-150}$$

and the increment in θ in going from the maximum to the minimum is

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[5] An improved version of the JWKB method has been given by Rosen et al. (1964); see also Kreiger et al. (1967).
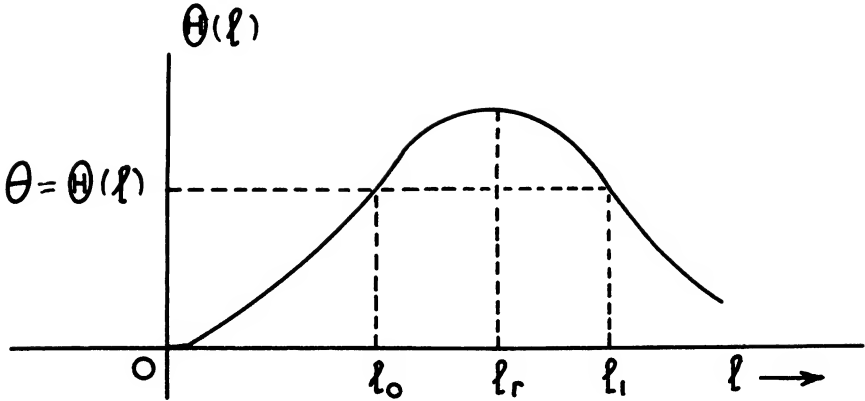
Figure 2-2 An example of the variation of the classical deflection function Θ with ℓ.

$$\delta\theta \simeq \frac{\pi}{|\ell_0 - \ell_1|}. \tag{2-151}$$

The angular difference $\delta\theta$ must be at least as large as the angle of resolution of the detecting system, or else the oscillations will not be observed.

The rainbow

When $\theta(\ell)$ is not a single valued function of ℓ, $\Theta(\ell)$ must possess either maxima or minima or singularities. In the example in figure 2, $d\Theta/d\ell = 0$ and Θ has a maximum at $\ell = \ell_r$ corresponding to a scattering angle θ_r. Any attractive monotonic potential, finite at the origin, will give rise to a curve with a minimum. because the deflection vanishes at $\ell = 0$ and $\ell = \infty$ and is negative in between. At a maximum or a minimum in $\Theta(\ell)$, the calculation of the cross section that we have given breaks down, because $\varphi_{\pm}''(\ell_r)$ which occurs in the integral (2-147) vanishes. When this happens in the corresponding optical situation a rainbow is produced, and the name rainbow scattering is also used to describe this phenomenon in the present context. The angle of scattering θ_r is called the rainbow angle.

Near the rainbow angle

$$\Theta(\ell) \simeq \theta_r + q(\ell - \ell_r)^2,$$ (2-152)

where $q = \dfrac{1}{2}\dfrac{d^2\Theta}{d\ell^2}\Big|_{\ell=\ell_r}$, and the phase shift δ_ℓ may be expan-

ded (using 2-139) as

$$\delta_\ell = \delta_{\ell_r} \pm \frac{1}{2}\theta_r(\ell - \ell_r) + \frac{q}{6}(\ell - \ell_r)^3.$$

It follows that the functions $\varphi_\pm$ are given by

$$\varphi_\pm(\ell) = 2\delta_{\ell_r} \pm \theta_r(\ell - \ell_r) + \frac{q}{3}(\ell - \ell_r)^3 \pm \left(\ell + \frac{1}{2}\right)\theta \pm \frac{\pi}{4}.$$

Instead of the integral (2-147), we now have

$$f_k(\theta) \simeq \left(\ell_r + \frac{1}{2}\right)^{\frac{1}{2}}\frac{1}{k}(2\pi\sin\theta)^{-\frac{1}{2}}e^{i\delta} \times$$

$$\times \int_{-\infty}^{\infty} e^{i[(\theta_r-\theta)(\ell-\ell_r)+(\ell-\ell_r)^3 q/3]}\,d(\ell - \ell_r),$$

where

$$\delta = 2\delta_{\ell_r} - \theta_r\left(\ell_r + \frac{1}{2}\right) \pm \frac{\pi}{4} \mp \left(\ell_r + \frac{1}{2}\right)(\theta_r - \theta).$$

The integral,

$$\text{Ai}(x) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{iux + iu^3/3}\,du,$$ (2-153)

is known as the Airy integral. For $x > 0$ (the dark side of the rainbow) $\text{Ai}(x)$ falls off rapidly, but for $x < 0$ (the bright side of the rainbow), $\text{Ai}(x)$ oscillates:

$$\text{Ai}(x) \sim \frac{3^{-1/3}}{2\sqrt{\pi}}x^{-\frac{1}{4}}e^{-(2/3)x^{3/2}}, \quad x \to +\infty$$

$$\sim \frac{3^{-1/3}}{\sqrt{\pi}}(-x)^{-\frac{1}{4}}\cos\left[\frac{2}{3}(-x)^{3/2} - \frac{\pi}{4}\right], \quad x \to -\infty. \quad (2-154)$$

The final expression for the cross section is

$$\frac{d\sigma}{d\Omega}(\theta \simeq \theta_r) = \frac{2\pi}{k^2}\left(\frac{\ell_r + 1/2}{\sin\theta}\right) q^{-\frac{2}{3}} \left| Ai\left(\frac{\theta_r - \theta}{q^{\frac{1}{3}}}\right)\right|^2 . \quad (2-155)$$

The glory

If $\Theta(\ell)$ passes smoothly through $\Theta = 0$ or $\theta = \pm\pi$, then $\sin\Theta(\ell)$ vanishes while $(d\Theta/d\ell)$ is finite. The classical cross section then becomes infinite $(2-147)$; this is termed a glory. In the evaluation of the cross section, the approximation $(2-140)$ for $P_\ell(\cos\theta)$ can no longer be used, because this is valid for $\sin\theta > 1/\ell$. Instead, the approximation for small $(\sin\theta)$,

$$P_\ell(\cos\theta) \sim (\cos\theta)^\ell J_0\left(\left(\ell + \frac{1}{2}\right)\theta\right),$$

is employed which is valid for $\sin\theta < 1/\ell$. If the glory occurs at $\ell = \ell_g$ and δ_ℓ is expanded about this value of ℓ,

$$\delta_\ell = \frac{\pi}{2}(\ell - \ell_g) + \frac{a}{4}(\ell - \ell_g)^2 + \delta_g, \quad (2-156)$$

where $a = \dfrac{d\Theta}{d\ell}\bigg|_{\ell=\ell_g}$, and the analysis can be extended to this

case. If the glory occurs in backward $\theta \simeq \pi$ it is found,

$$\frac{d\sigma}{d\Omega}(\theta) = \frac{1}{k^2}\left(\ell_g + \frac{1}{2}\right)^2 \frac{2\pi}{|a|} J_0^2(\ell_g \sin\theta). \quad (2-157)$$

The classical singularity is replaced by a finite peak at $\theta = \pi$ and as θ is decreased, the cross section oscillates rapidly.

Orbiting

Classically the scattered particle may be caught on an orbit that spirals infinitely, tending ultimately to a circular orbit. In this case, the deflection function exhibits a singularity at some value of ℓ. This is called orbiting and is well known in collisions between rare gas atoms and ions. As might be expected, the phenomenon is extremely complicated and it will not be described here. The theory may be consulted in the original papers by Ford and Wheeler (1959).

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Chapter 3   .

SCATTERING BY LONG RANGE POTENTIALS

Various aspects of the theory outlined in Chapters 1 and 2 must be modified when the potential decreases like an inverse power of r, for large r. In the important case of Coulomb scattering for which $V(r) = a/r$, the boundary conditions satisfied by the wave function at large r are different from those assumed in Chapter 1 and although potentials decreasing like r^{-1-n} with $n > 0$, do satisfy the normal boundary conditions at infinity, the important effective range formulae for the phase shifts cease to apply.

3-1   COULOMB SCATTERING

When the target and scattered particles are charged, a Coulomb potential acts between them which, at small distances of separation, will be modified by other effective interactions, that in general decrease as some higher inverse power of r. In actual experiments, the Coulomb interaction will not extend to infinite distances, but will be shielded by the other atoms in the target. The shielding has the effect of cutting off the potential at some distance R, and to a good approximation the potential will be of the form

$$V(r) = a/r, \quad r < R,$$
$$V(r) = 0, \quad r > R,$$

(3-1)

where R is of dimension comparable to the spacing of the

atoms in the target. Since the problem of Coulomb scattering can be solved exactly it is useful to ignore the shielding effects at the start, and subsequently it will be shown that they are not important in practice.

The Schrödinger equation for scattering by a pure Coulomb potential is

$$(\nabla^2 + k^2 - a/r)\Psi(\mathbf{r}) = 0, \tag{3-2}$$

where if $(Z_1 e)$, $(Z_2 e)$ are the charges of the target and scattered particles, $a = (2mZ_1 Z_2 e^2/\hbar^2)$. This equation is separable in parabolic coordinates (details can be found in Landau and Lifshitz, 1958, p. 125), defined by

$$\xi = r + z, \; \eta = r - z, \; \varphi = \tan^{-1}\left(\frac{y}{x}\right), \tag{3-3}$$

where x, y and z are the usual Cartesian coordinates and $r^2 = x^2 + y^2 + z^2$. The coordinates ξ and η range from 0 to ∞ and φ ranges from 0 to (2π). The Schrödinger equation in parabolic coordinates is

$$\left(\frac{4}{\xi + \eta}\right)\left[\frac{\partial}{\partial \xi}\left(\xi \frac{\partial \Psi}{\partial \xi}\right) + \frac{\partial}{\partial \eta}\left(\eta \frac{\partial \Psi}{\partial \eta}\right)\right] + \frac{1}{\xi \eta}\frac{\partial^2 \Psi}{\partial \varphi^2} + \left[k^2 - \frac{2a}{\xi + \eta}\right]\Psi = 0. \tag{3-4}$$

The equation may be separated by writing

$$\Psi = f_1(\xi)f_2(\eta)e^{im\varphi}, \tag{3-5}$$

but because of the symmetry about the z axis (which is taken as the direction of incidence), only the case $m = 0$ need be considered. Then $f_1(\xi)$ and $f_2(\eta)$ satisfy

$$\frac{d}{d\xi}\left(\xi \frac{df_1}{d\xi}\right) + \left(\frac{1}{4}k^2\xi + \beta\right)f_1 = 0,$$
$$\frac{d}{d\eta}\left(\eta \frac{df_2}{d\eta}\right) + \left(\frac{1}{4}k^2\eta - \beta - \frac{a}{2}\right)f_2 = 0, \tag{3-6}$$

where β is a constant of separation.

A solution is required that behaves like the plane wave $\exp(ikz)$, as $z \to -\infty$ and $r \to +\infty$. In terms of ξ and η, the incident plane wave looks like

$$\exp(ikz) = \exp(ik(\xi - \eta)/2), \tag{3-7}$$

and Ψ must behave like this as $\eta \rightarrow \infty$ (all ξ).

This condition can be satisfied by taking $\beta = -\frac{1}{2}ik$, in which case

$$f_1(\xi) = e^{ik\xi/2}. \tag{3-8}$$

The equation for $f_2(\eta)$ then becomes

$$\frac{d}{d\eta}\left(\eta\frac{df_2}{d\eta}\right) + \left(\frac{1}{4}k^2\eta - \frac{1}{2}a + \frac{1}{2}ik\right)f_2 = 0. \tag{3-9}$$

To satisfy the boundary condition, we set

$$f_2(\eta) = e^{-\frac{1}{2}ik\eta}w(\eta), \tag{3-10}$$

and look for a solution such that $w(\eta) \rightarrow$ constant, as $\eta \rightarrow \infty$. The new function $w(\eta)$ satisfies

$$\eta\frac{d^2w}{d\eta^2} + (1 - ik\eta)\frac{dw}{d\eta} - \left(\frac{a}{2}\right)w = 0. \tag{3-11}$$

This is the equation satisfied by the confluent hypergeometric function defined by the expansion (Morse and Feshbach, 1953, p. 551; Landau and Lifshitz, 1958, p. 600),

$$F(a,b,x) = \sum_{n=0}^{\infty} \frac{\Gamma(a + n)\Gamma(b)}{\Gamma(b + n)\Gamma(a)} \frac{x^n}{n!}. \tag{3-12}$$

This function is the solution, regular at the origin, of the equation

$$x\frac{d^2F}{dx^2} + (b - x)\frac{dF}{dx} - aF = 0, \tag{3-13}$$

so that the parameters a and b and the variable x must be identified by the relations

$$a = -ia/2k, \quad b = 1, \quad x = ik\eta. \tag{3-14}$$

In terms of spherical polar coordinates the solution of the original Schrödinger equation is

$$\Psi_{\mathbf{k}}^{c^+}(\mathbf{r}) = Ce^{ikz}F(-ia/2k, 1, ikr(1 - \cos\theta)), \tag{3-15}$$

where C is a constant. The asymptotic form of the confluent hypergeometric function is, for large x,

$$F(a,b,x) \sim \frac{\Gamma(b)}{\Gamma(b-a)} e^{-a \log(-x)} \left[1 + \frac{a(a+1-b)}{x} + \ldots \right] +$$

$$+ \frac{\Gamma(b)}{\Gamma(a)} e^{x+(a-b)\log x} \left[1 + \frac{(1-a)(b-a)}{x} + \ldots \right],$$

$$(3-16)$$

and hence the asymptotic form of the wave function is

$$\Psi_k^{c+}(\mathbf{r}) \sim C \frac{e^{a\pi/4k}}{\Gamma(1+ia/2k)} \left[\left\{ 1 - \frac{a^2}{4ik^3 r(1-\cos\theta)} \right\} e^{i[kz +} \right.$$

$$\left. + (a/2k)\log kr(1-\cos\theta)] + f_k^c(\theta) r^{-1} e^{i[kr - (a/2k)\log 2kr]} \right],$$

$$(3-17)$$

where the scattering amplitude is

$$f_k^c(\theta) = - \frac{a}{4k^2 \sin^2\theta/2} \frac{\Gamma(1+ia/2k)}{\Gamma(1-ia/2k)} e^{-i(a/2k)\log \sin^2\theta/2}. \quad (3-18)$$

It should be noticed that the asymptotic form is valid for sufficiently large r, except in the forward direction where $\cos\theta = 1$. Because of the slow decrease of the potential as r increases the incident wave is distorted by logarithmic phase factors which, of course, do not alter the flux at large distances (to order $1/r^2$).

If $C = \Gamma(1 + ia/2k) e^{-a\pi/4k}$ the normalization is such that the flux of the incident wave is $F = \hbar k/m$. The normalization of the wave function $\Psi_k^{c+}(\mathbf{r})$ is then

$$\int \Psi_{k'}^{c+*}(\mathbf{r}) \Psi_k^{c+}(\mathbf{r}) d\mathbf{r} = (2\pi)^3 \delta(\mathbf{k'} - \mathbf{k}),$$

and the closure relation is

$$\left(\frac{1}{2\pi} \right)^3 \int d\mathbf{k} \, \Psi_k^{c+*}(\mathbf{r'}) \Psi_k^{c+}(\mathbf{r}) + \sum_i \varphi_i^*(\mathbf{r'}) \varphi_i(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r'}),$$

where the sum over i occurs only in the case of an attractive potential ($a < 0$) and the $\varphi_i(\mathbf{r})$ are the bound state wave functions, normalized to unity.

The differential cross section,

$$\frac{d\sigma}{d\Omega} = |f^c_k(\theta)|^2 = \frac{a^2}{16k^4 \sin^4 \theta/2} , \qquad (3\text{-}19)$$

is identical with the classical expression obtained in Chapter 2, but the phase of the amplitude is naturally not given by classical mechanics and is important in several situations. For example if the target and scattered particles are identical, the wave function must either be symmetric or anti-symmetric in the coordinates of the two particles and in the center of mass system, the wave function must be of the form

$$\Phi(r,\theta) = \Psi(r,\theta) \pm \Psi(r, \pi - \theta), \qquad (3\text{-}20)$$

where $\Psi(r,\theta)$ is the solution of the Schrödinger equation with the usual boundary conditions for elastic scattering. The detector cannot distinguish between particles that have scattered and those which have recoiled, so that the cross-section is

$$\frac{d\sigma}{d\Omega} = |f(\theta) \pm f(\pi - \theta)|^2 . \qquad (3\text{-}21)$$

For Coulomb scattering between two spinless charged particles, the total wave function must be symmetrical and the upper sign should be taken, giving the Mott formula

$$\frac{d\sigma}{d\Omega} = \frac{a^2}{16k^4 \sin \theta/2}\left[1 + \tan^4 \theta/2 + 2\tan^2\theta/2 \cos\left(\frac{a}{2k} \log\tan^2 \theta/2\right)\right],$$

$$(3\text{-}22)$$

where the last term results from interference between the two amplitudes and depends directly on the phase.

Bound states

For an attractive potential, the scattering amplitude is expected to have poles at the energies of the bound states (Section 1-7). This immediately follows from the form (3-18), because the function $\Gamma(1 - ia/2k)$ has zeros located at the points where

$$k^2 = -a^2/4n^2, \quad n = 1,2,3 \ldots , \qquad (3\text{-}23)$$

and these coincide with the bound state energies of a particle in a Coulomb potential.

Shielding

Examining the asymptotic form of the wave function, it is seen that if the Coulomb potential is cut off as in equation (3-1) at a distance R then, provided $(a^2/k^3) \ll R (1 - \cos \theta)$, the scattering amplitude will be altered only by a logarithmic phase factor

$$f_{\mathbf{k}}(\theta) = f_{\mathbf{k}}^{c}(\theta) e^{-ia[\log(2kR)]/2k}$$

and the cross-section is unaltered by the cut-off. Under experimental conditions the range of angles, $\theta < a/(k^3 R)^{\frac{1}{2}}$, for which terms in the wave function of order $1/R$ become significant, is small compared with angular acceptance of detectors and can be ignored. A complete discussion of the scattering amplitude for the screened Coulomb potential has been given by Ford (1964, 1966).

3-2   PARTIAL WAVE EXPANSION OF COULOMB AMPLITUDES

The Coulomb wave function can be expanded in a series of Legendre polynomials as in (1-19) and the radial wave functions satisfy the equation

$$\left(\frac{d^2}{dr^2} + k^2 - \frac{a}{r} - \frac{\ell(\ell + 1)}{r^2} \right) f_{\ell}^{c}(r) = 0. \qquad (3-24)$$

This can be reduced to the equation satisfied by the confluent hypergeometric function by the substitution

$$f_{\ell}^{c}(r) = r^{\ell+1} e^{ikr} H_{\ell}(r), \qquad (3-25)$$

we find

$$r \frac{d^2 H_{\ell}}{dr^2} + 2(\ell + 1 + ikr) \frac{dH_{\ell}}{dr} + [2ik(\ell + 1) - a] H_{\ell} = 0. \qquad (3-26)$$

A further change of variable to $\rho = -2ikr$ gives

$$\rho \frac{d^2 H_{\ell}}{d\rho^2} + (2\ell + 2 - \rho) \frac{dH_{\ell}}{d\rho} + \left[\frac{a}{2ik} - (\ell + 1) \right] H_{\ell} = 0, \qquad (3-27)$$

and comparing (3.27) with (3.13), the solution regular at the origin is found to be

$$H_\ell(\rho) = F(ia/2k + \ell + 1, 2\ell + 2, \rho). \tag{3-28}$$

The required solution for the radial function is

$$f_\ell^C(r) = A_\ell r^{\ell+1} e^{ikr} F(\ell + 1 + ia/2k, 2\ell + 2, -2ikr), \tag{3-29}$$

where A_ℓ is a constant.

The asymptotic form of f_ℓ^C can be found from equation (3-16):

$$f_\ell^C(r) \sim A_\ell e^{\pi a/4k} \frac{\Gamma(2\ell + 2)}{|\Gamma(\ell + 1 + ia/2k)|} 2^{-\ell} k^{-(\ell+1)} \times$$

$$\times \sin(kr - \tfrac{1}{2}\ell\pi + \sigma_\ell - (a/2k) \log 2kr), \tag{3-30}$$

where the Coulomb phase shifts σ_ℓ are defined as

$$\sigma_\ell = \arg \Gamma(\ell + 1 + ia/2k). \tag{3-31}$$

A standard solution may be defined as $F_\ell(r)$, with the normalization

$$F_\ell(r) \sim \sin(kr - \tfrac{1}{2}\ell\pi + \sigma_\ell - a/2k \log 2kr), \tag{3-32}$$

in which case

$$F_\ell(r) = e^{-\pi a/(4k)} \frac{|\Gamma(\ell + 1 + ia/2k)|}{(2\ell + 1)!} 2^\ell (kr)^{\ell+1} e^{ikr} \times$$

$$\times F(\ell + 1 + ia/2k, 2\ell + 2, -2ikr). \tag{3-33}$$

The expansion of the complete Coulomb function in terms of the partial wave functions is

$$\Psi_{\mathbf{k}}^{c+} = \sum_{\ell=0}^{\infty} (2\ell + 1)(kr)^{-1} e^{i\sigma_\ell} F_\ell(r) i^\ell P_\ell(\cos\theta). \tag{3-34}$$

An independent solution of the radial equation is often required and it has been shown by Yost, Wheeler and Breit (1936) that a second solution $G_\ell(r)$ of equation (3-24), irregular at the origin, can be found that has the asymptotic form

$$G_\ell(r) \sim \cos\left(kr - \tfrac{1}{2}\ell\pi + \sigma_\ell - (a/2k)\log(2kr)\right). \tag{3-35}$$

A very complete discussion of the many interesting properties of F_ℓ and G_ℓ may be consulted in the article by Hull and Breit (1959), where methods of numerical calculation of these functions are described and references are given to existing tabulations.

Scattering by a modified Coulomb potential

Consider the scattering by a potential $V(r)$ which is of the form

$$U(r) = \frac{2m}{k^2} V(r) = U_1(r) + a/r, \qquad (3-36)$$

where $U_1(r)$ is of short range. The asymptotic solution of the radial wave equation regular at the origin must be a linear combination of F_ℓ and G_ℓ, and it is natural to define a phase shift δ_ℓ in a similar way to (1-50) by requiring that the solution of the radial wave equation has the asymptotic form

$$f_\ell(r) \sim F_\ell(r) + \tan \delta_\ell G_\ell(r). \qquad (3-37)$$

The phase shifts δ_ℓ will then characterize the short range potential $U_1(r)$, although it is important to notice that the δ_ℓ are not quite the same as phase shifts that would be obtained if a were set to zero.

To find the connection between the phase shifts δ_ℓ and the scattering amplitude, the solution $\Psi(\mathbf{r})$ of the Schrödinger equation is introduced, where

$$\Psi(\mathbf{r}) = \sum_{\ell=0}^{\infty} (2\ell+1) i^\ell (kr)^{-1} e^{i(\sigma_\ell+\delta_\ell)} \cos \delta_\ell f_\ell(r) P_\ell(\cos \theta). \qquad (3-38)$$

To find the asymptotic form of this solution, consider the difference $[\Psi(\mathbf{r}) - \Psi_{\mathbf{k}}^{c+}(\mathbf{r})]$ where $\Psi_{\mathbf{k}}^{c+}(\mathbf{r})$ is the wave function for scattering by the Coulomb potential alone; we have

$$\left[\Psi(\mathbf{r}) - \Psi_{\mathbf{k}}^{c+}(\mathbf{r})\right] \sim \sum_{\ell=0}^{\infty} \frac{(2\ell+1) i^\ell}{(kr)} \left[e^{i(\sigma_\ell+\delta_\ell)} \cos \delta_\ell \left(F_\ell + \tan \delta_\ell G_\ell \right) \right.$$

$$\left. - e^{i\sigma_\ell} F_\ell(r) \right] P_\ell(\cos \theta). \qquad (3-39)$$

From the asymptotic forms of F_ℓ and G_ℓ, we find that

$$\left[\Psi(\mathbf{r}) - \Psi_{\mathbf{k}}^{c^+}(\mathbf{r}) \right] \sim f_1(\theta) r^{-1} e^{i(kr - a/2k \log 2kr)}$$

where

$$f_1(\theta) = \sum_{\ell=0}^{\infty} (2\ell + 1) \frac{1}{2ik} e^{2i\sigma_\ell} (e^{2i\delta_\ell} - 1) P_\ell(\cos \theta).$$

$$(3-40)$$

Using the asymptotic form of $\Psi_{\mathbf{k}}^{c^+}(\mathbf{r})$, equation (3-17), we obtain

$$\Psi(\mathbf{r}) \sim e^{i(kz + a/2k \log kr(1-\cos \theta))} + \left[f_{\mathbf{k}}^{c}(\theta) + \right.$$

$$\left. + f_1(\theta) \right] r^{-1} e^{i(kr - a/2k \log 2kr)}, \qquad (3-41)$$

where $f_{\mathbf{k}}^{C}$ is the Coulomb scattering amplitude. $\Psi(\mathbf{r})$ represents an incident wave of unit amplitude and an outgoing wave of amplitude $[f_{\mathbf{k}}^{C}(\theta) + f_1(\theta)]$ and the differential cross section is

$$\frac{d\sigma}{d\Omega} = | f_{\mathbf{k}}^{C}(\theta) + f_1(\theta)|^2. \qquad (3-42)$$

The partial wave series $f_1(\theta)$ converges rapidly, as the rate of convergence depends on the phase shifts δ_ℓ which relate to the short range potential. The partial wave series for $f_{\mathbf{k}}^{C}(\theta)$ does not converge and the unexpanded form of $f_{\mathbf{k}}^{C}(\theta)$, (3-18), must always be used.

The zero order Coulomb phase shift, which is given by

$$e^{2i\sigma_0} = \frac{\Gamma(1 + ia/2k)}{\Gamma(1 - ia/2k)}, \qquad (3-43)$$

can be removed from both $f_{\mathbf{k}}^{C}(\theta)$ and $f_1(\theta)$. If this is done

$$\frac{d\sigma}{d\Omega} = | \bar{f}^{C}(\theta) + \bar{f}_1(\theta)|^2, \qquad (3-44)$$

where

$$\bar{f}^{C}(\theta) = - \frac{a}{4k^2 \sin^2 \theta/2} e^{-i(a/2k)\log \sin^2 \theta/2},$$

and

$$\bar{f}_1(\theta) = \sum_\ell (2\ell + 1) \frac{1}{2ik} e^{2i(\sigma_\ell - \sigma_o)}\left(e^{2i\delta_\ell} - 1\right) P_\ell(\cos\,\theta).$$

$$(3-45)$$

The phase shift difference $(\sigma_\ell - \sigma_o)$ can be easily determined using the recurrence relation

$$(\sigma_{\ell+1} - \sigma_\ell) = \arg\,\Gamma\left(\ell + 2 + \frac{ia}{2k}\right) - \arg\,\Gamma\left(\ell + 1 + \frac{ia}{2k}\right)$$

$$= \arg\left(\ell + 1 + \frac{ia}{2k}\right) = \tan^{-1}\left(\frac{a}{2k(\ell+1)}\right).(3-46)$$

3-3   GREEN'S FUNCTIONS FOR COULOMB SCATTERING

The equation for scattering by a modified Coulomb potential, such as (3-36), can be turned into an integral equation incorporating the required boundary conditions. The radial Schrödinger equation for scattering in the ℓth partial wave is

$$\left(\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2} - \frac{a}{r} + k^2\right) f_\ell(r) = U_1(r) f_\ell(r),\qquad (3-47)$$

and a solution is required with asymptotic form (3-37). The integral equation for $f_\ell(r)$ can be written as

$$f_\ell(r) = F_\ell(r) + \int_0^\infty dr' g_\ell^C(r,r') U_1(r') f_\ell(r'),\qquad (3-48)$$

and it can be verified by substitution that $f_\ell(r)$ satisfies the radial Schrödinger equation (3-47), if $g_\ell^C(r,r')$ is

$$g_\ell^C(r,r') = -\frac{1}{k} F_\ell(r_<) G_\ell(r_>).\qquad (3-49)$$

In obtaining this result it is necessary to use the Wronskian relation

$$\frac{dF_\ell}{dr} G_\ell - \frac{dG_\ell}{dr} F_\ell = k.\qquad (3-50)$$

The asymptotic form of $f_\ell(r)$ satisfies equation (3-37) and the

phase shift δ_ℓ is determined by

$$\tan \delta_\ell = -\frac{1}{k} \int_0^\infty F_\ell(r) U_1(r) f_\ell(r) dr .\tag{3-51}$$

The analogue of the Born approximation, sometimes called the Coulomb–Born approximation, is obtained if $f_\ell(r)$ is replaced by $F_\ell(r)$ in (3-51),

$$\tan \delta_\ell^B = -\frac{1}{k} \int_0^\infty [F_\ell(r)]^2 U_1(r) dr .\tag{3-52}$$

Note that the Green's function g_ℓ^C satisfies the equation

$$\left(\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2} + k^2 - \frac{a}{r}\right) g_\ell^C(r,r') = \delta(r - r') .$$

Instead of imposing standing wave boundary conditions, Green's functions can be defined to satisfy outgoing wave boundary conditions

$$g_\ell^{C\pm}(r,r') = -\frac{1}{k} F_\ell(r_<)\left[G_\ell(r_>) \pm iF_\ell(r_>)\right],\tag{3-53}$$

from which it is easy to show that

$$T_\ell(k) = e^{i\delta_\ell} \sin \delta_\ell = -\frac{1}{k} \int_0^\infty F_\ell(r) U_1(r) f_\ell^+(r) dr ,\tag{3-54}$$

where $f_\ell^+(r)$ is a solution of the radial Schrödinger equation satisfying the boundary condition

$$f_\ell^+(r) \sim F_\ell(r) + T_\ell[iF_\ell(r) + G_\ell(r)] .\tag{3-55}$$

The Green's function for the operator $(\nabla^2 + k^2 - a/r)$ can be obtained in closed form by summing a Legendre polynomial series with the coefficients g_ℓ^C, or otherwise (Schwinger, 1964; Hostler, 1964). The Green's function for a shielded Coulomb potential has also been obtained by Ford (1964, 1966). From these Green's functions an integral equation can be found for the scattering amplitude $f_1(\theta)$, appearing in (3-41). Rather than construct the Green's function explicitly, we shall derive a general expression for the scattering amplitude for scattering by the sum of two potentials.

Scattering by the sum of two potentials

A convenient expression can be obtained for the scattering amplitude when the potential V is the sum of two terms $(V_1 + V_2)$, for one of which the solution of the Schrödinger equation is known exactly. One of the potentials may be a screened Coulomb potential and the final result will also be true when one of the potentials is an unscreened Coulomb potential.

Let $|\chi_{\mathbf{k}}^{\pm}\rangle$ be the solution of the Schrödinger equation,

$$(H_0 + V_1 - E)|\chi_{\mathbf{k}}^{\pm}\rangle = 0, \tag{3-56}$$

then the corresponding integral equation for $|\chi_{\mathbf{k}}^{\pm}\rangle$ is

$$|\chi_{\mathbf{k}}^{\pm}\rangle = |\varphi_{\mathbf{k}}\rangle + G_0^{\pm}V_1|\chi_{\mathbf{k}}^{\pm}\rangle \tag{3-57a}$$

$$= (1 + G_1^{\pm}V_1)|\varphi_{\mathbf{k}}\rangle. \tag{3-57b}$$

where as usual $|\varphi_{\mathbf{k}}\rangle$ is the state vector for the incident unperturbed state, $G_0^{\pm}$ is the free particle Green's operator and and G_1 is the complete Green's operator for the potential V_1,

$$G_1^{\pm} = (E \pm i\epsilon - H_0 - V_1)^{-1}. \tag{3-58}$$

If $|\Psi_{\mathbf{k}}^{\pm}\rangle$ is the state vector for scattering from the potential $(V_1 + V_2)$, it satisfies

$$(H_0 + V_1 + V_2 - E)|\Psi_{\mathbf{k}}^{\pm}\rangle = 0. \tag{3-59}$$

The solution of this equation can now be written in terms of the Green's operator, G_1. A solution with the correct boundary conditions is

$$|\Psi_{\mathbf{k}}^{\pm}\rangle = |\chi_{\mathbf{k}}^{\pm}\rangle + G_1^{\pm}V_2|\Psi_{\mathbf{k}}^{\pm}\rangle. \tag{3-60}$$

The scattering amplitude for scattering by the combined potential $f_{\mathbf{k}}(\theta)$ is given by

$$f_{\mathbf{k}}(\theta) = -\left(\frac{2m}{\hbar^2}\right) \frac{1}{4\pi} T(\mathbf{k} \rightarrow \mathbf{k}'), \qquad (3-61)$$

where

$$T(\mathbf{k} \rightarrow \mathbf{k}') = \langle \varphi_{\mathbf{k}'} | V_1 + V_2 | \Psi_{\mathbf{k}}^+ \rangle.$$

Using the integral equation for $|\Psi_{\mathbf{k}}^+\rangle$ we find that

$$T(\mathbf{k} \rightarrow \mathbf{k}') = \langle \varphi_{\mathbf{k}'} | V_1 | \chi_{\mathbf{k}}^+ \rangle + \langle \varphi_{\mathbf{k}'} | (V_1 G_1^+ + 1) V_2 | \Psi_{\mathbf{k}}^+ \rangle$$

$$= \langle \varphi_{\mathbf{k}'} | V_1 | \chi_{\mathbf{k}}^+ \rangle + \langle \chi_{\mathbf{k}'}^- | V_2 | \Psi_{\mathbf{k}}^+ \rangle, \qquad (3-62)$$

where in the second line the adjoint of equation (3-57b) has been employed. The first term on the right hand side of (3-62) is the transition matrix element for scattering from the potential V_1 by itself. If V_1 is the Coulomb potential and V_2 a short range potential, then the result expressed in equations (3-41) and (3-42) is recovered

$$f(\theta) = f^C(\theta) + f_1(\theta),$$

where $f_{\mathbf{k}}^C(\theta)$ is the Coulomb scattering amplitude. In this example $\langle \chi_{\mathbf{k}}^- | \mathbf{r} \rangle$ is the complex conjugate of the Coulomb wave function $\Psi_{\mathbf{k}}^{c-}(\mathbf{r})$ where

$$\Psi_{\mathbf{k}}^{c-}(\mathbf{r}) = e^{-\alpha\pi/4k} \Gamma\left(1 - \frac{i\alpha}{2k}\right) e^{ikz} F\left(\frac{i\alpha}{2k}, 1, -ikr(1 + \cos\theta)\right).$$

$$(3-63)$$

The asymptotic form of $\Psi_{\mathbf{k}}^{c-}(\mathbf{r})$ is that of an incident plane wave and an incoming spherical wave, modified by the usual logarithmic phase factors. The scattering amplitude $f_1(\theta)$ is then

$$-(4\pi) f_1(\theta) = \int d\mathbf{r} \, \Psi_{\mathbf{k}'}^{c-*}(\mathbf{r}) U_2(\mathbf{r}) \Psi_{\mathbf{k}}^+(\mathbf{r}), \qquad (3-64)$$

where $U_2(\mathbf{r}) = 2mV_2/\hbar^2$.

3-4   SCATTERING AT VERY LOW ENERGIES AND LONG RANGE POTENTIALS

The effective range formulae must be modified when the potential varies like an inverse power of r for large r. For short range potentials the variation of the phase shift with momentum was derived from equation (1-58). It is clear that the integral,

$$\int_0^\infty r^{2\ell+2} U(r) dr,$$

occurring in that equation will only converge if the potential decreases faster than $r^{-(2\ell+3)}$, for large r. For a potential decreasing less fast than $1/r^3$, the limit $k \to 0$ of $(\delta_\ell/k^{2\ell+1})$ does not exist for any ℓ and no scattering lengths can be defined. For a potential decreasing like $(1/r^4)$, the scattering length for $\ell = 0$ exists, but the scattering lengths for higher ℓ do not. The condition for the existence of the effective ranges is more restrictive, and it is necessary for the potential to decrease faster than $r^{-(2\ell+5)}$ for these quantities to be defined.

The modified Coulomb potential

An effective range formulae for the phase shift δ_0 describing scattering from a short range potential in the presence of a Coulomb field can be obtained by using the Wronskian relations discussed in Chapter 1. Consider the solutions of the Schrödinger equation (3-47), $f_\ell(k,r)$, with the boundary conditions (for $\ell = 0$),

$$f_0(k,0) = 0, \quad f_0(k,r) \sim F_0(r) \cot \delta_0 + G_0(r), \qquad (3-65)$$

where F_0 and G_0 are the regular and irregular Coulomb functions. By considering the radial Schrödinger equations for different energies k_1^2 and k_2^2, but the same potential, it is easy to follow an argument similar to that leading to (1-45), and to show that

$$\left[f_0(k_1,r)\frac{d}{dr}f_0(k_2,r) - f_0(k_2,r)\frac{d}{dr}f_0(k_1,r)\right]_0^r$$

$$= \left[k_1^2 - k_2^2\right]\int_0^r f_0(k_1,r)f_0(k_2,r)dr. \qquad (3\text{-}66)$$

A similar equation can be written for the function

$$h_0(k,r) \equiv F_0(r)\cot\delta_0 + G_0(r),$$

and on subtracting the equations for f_0 and h_0, we find (remembering that $f_0(k,0) = 0$)

$$\lim_{r\to 0}\left[h_0(k_1,r)\frac{d}{dr}h_0(k_2,r) - h_0(k_2,r)\frac{d}{dr}h_0(k_1,r)\right]$$

$$= (k_1^2 - k_2^2)\int_0^\infty \left(f_0(k_1,r)f_0(k_2,r) - h_0(k_1,r)h_0(k_2,r)\right)dr.$$

To evaluate the left hand side, the expansions of G_0 and F_0 are required for small r. From the series expansion of the confluent hypergeometric function, it can easily be seen that for small r,

$$F_0(r) \to (kr)e^{-\pi a/4k}\left|\Gamma\left(1 + \frac{ia}{2k}\right)\right| = (kr)C(k), \qquad (3\text{-}67)$$

where

$$C^2(k) = \frac{\pi a}{k(e^{\pi a/k} - 1)}.$$

Yost et al. (1936) have obtained the following form for $G_0(kr)$ at small r,

$$G_0(r) = C^{-1}\left[1 + ar\left\{\log ar - 1 + \gamma + \sum_{s=1}^\infty \frac{a^2/4k^2}{s(s^2 + a^2/4k^2)} - \log\frac{a}{2k}\right\}\right], \qquad (3\text{-}68)$$

where $\gamma = 0.577\ldots$ is Euler's constant.

On using these expressions and multiplying by $C(k_1)\ C(k_2)$ we obtain

$$- C^2(k_1)k_1 \cot \delta_0(k_1) - a\varphi(k_1) + C^2(k_2)k_2 \cot \delta_0(k_2) + a\varphi(k_2)$$

$$= (k_1^2 - k_2^2)C(k_1)C(k_2) \int_0^\infty \Big(f_0(k_1,r)f_0(k_2,r) - h_0(k_1,r)h_0(k_2,r) \Big) dr,$$

$$(3-69a)$$

where

$$\varphi(k) = +\gamma - \log\Big(\frac{a}{2k}\Big) + \sum_{s=1}^\infty \frac{a^2/4k^2}{s(s^2 + a^2/4k^2)}. \qquad (3-69b)$$

Taking the limit $k_1 \to k_2$, we find

$$\frac{d}{d(k^2)}\{kC^2(k)\cot \delta_0 + a\varphi(k)\} = C^2(k) \int_0^\infty \Big(-f_0^2(k,r) + h_0^2(k,r)\Big)dr.$$

Then expanding $\{kC^2 \cot \delta_0 + a\varphi(k)\}$ in a Taylor's series in k^2, about $k^2 = 0$, the effective range expansion is obtained as

$$kC^2 \cot \delta_0 + a\varphi(k) = \frac{1}{a_s} + \frac{1}{2}r_0 k^2 + \dots , \qquad (3-70)$$

where

$$r_0 = \lim_{k \to 0} 2C^2(k) \int_0^\infty \Big(-f_0^2(k,r) + h_0^2(k,r)\Big)dr. \qquad (3-71)$$

This effective range expansion can be generalized to all ℓ; it is found (Biberman and Norman, 1963),

$$N_\ell^2 \left\{ C^2 k \cot \delta_\ell - a\left[\varphi(k) + \sum_{s=0}^\ell \frac{s}{s^2 + a^2/4k^2} \right] \right\}$$

$$= \frac{1}{a_{s_\ell}} + \frac{1}{2}r_\ell k^2 + \dots , \qquad (3-72)$$

where

$$N_\ell^2 = \prod_{s=1}^\ell \Big(k^2 + \frac{a^2}{4s^2}\Big), \quad N_0 = 1.$$

Quantum defects

For an attractive Coulomb potential the S-matrix elements have poles at the bounds states, which occur at

$k = i\lambda$, with $\lambda^2 = (a/2.n)^2$, $n = 1, 2, \ldots$. When a short range potential modifies the Coulomb potential, the energy levels will be shifted. This can be taken into account by writing

$$E_{n,\ell} = -\frac{\hbar^2}{2m}\lambda^2, \quad \lambda^2 = \frac{a^2}{4(n - \mu_{n,\ell})^2} . \tag{3-73}$$

The constants $\mu_{n,\ell}$ are known as quantum defects. At the bound states, $\cot \delta_\ell = i$, (Section 1-7), and inserting $k_2^2 = -\lambda^2$ and $\cot \delta_0(k_2) = i$ in (3-69a), Seaton (1955) showed that

$$\cot \delta_0(k) = [1 - e^{-\pi a/k}]\cot\left(\pi\mu_0(k)\right), \tag{3-74}$$

where the quantum defect $\mu_0(k)$ is considered as a function of energy interpolating between the bound state positions (where it is defined by (3-73)) and extrapolated to positive energies.

This relation may be used to estimate, for example, the phase shifts for electron scattering by helium ions. The energy levels of the (1s, ns) series of He are known, and from these the interpolating function $\mu_0(k)$ can be computed. On extrapolating this function to positive energies, the phase shifts for electron scattering by the (1s) state of He$^+$ can be estimated (Seaton, 1957).

Inverse power potentials

The interaction between a charged particle and a neutral polarizable system, such as an atom or molecule, varies like $(1/r^4)$ at large distances. The Van der Waals interaction between two neutral polarizable systems varies as $(1/r^6)$ at large r and in certain circumstances interactions varying like $(1/r^3)$ can also be of importance in atomic physics. These long range interactions modify the threshold behaviour of cross sections and, as we have already noted, the usual effective range formulae will not always hold.

It is important that in actual applications the inverse power law of the potential is not followed down to the origin, because if this were so, difficulties could arise in defining a solution of the Schrödinger equation. This may be seen as follows in the case of a potential varying as a/r^3. For small

r, provided k^2 is finite, the radial Schrödinger equation is

$$\left(\frac{d^2}{dr^2} - \frac{\ell(\ell + 1)}{r^2} - \frac{a}{r^2}\right)f_\ell(r) = 0,\tag{3-75}$$

where a is the potential strength and where k^2 has been neglected compared with $1/r^2$. Expanding $f_\ell(r)$ as a power series

$$f_\ell(r) = \sum_{i=M}^{\infty} C_i r^{i+1},\tag{3-76}$$

the indicial equation becomes

$$M(M + 1) = [\ell(\ell + 1) + a],\tag{3-77}$$

with the solution

$$M_\pm = \frac{1}{2}\left[-1 \pm \{1 + 4\ell(\ell + 1) + 4a\}^{\frac{1}{2}}\right].\tag{3-78}$$

When a is positive and the potential repulsive, if the lower sign is taken the solution $f_0(r)$ is irregular and can be rejected. For attractive potentials with $4a < -1$, both M_+ and M_- are complex, while if $-1 < 4a < 0$, both M_+ and M_- are negative. In the latter case, the solution with the lower singularity at the origin could be taken as scattering solution, but in the former, the two solutions are complex conjugates of one another and there is no means of determining which should be taken. In general it may be shown that a regular solution exists for all repulsive inverse power potentials, but a scattering solution cannot be defined for the corresponding attractive potentials, if these potentials continue down to the origin.

If the potential satisfies the condition $r^2 U(r) \to 0$ as $r \to 0$ but behaves like an inverse power of r for large r, no difficulty in defining a solution occurs, because at small r the radial equation is dominated by the centrifugal barrier $\ell(\ell + 1)/r^2$. If the potential is exactly of the form a/r^2 for $r > r_0$, then at zero energy, the radial wave function will satisfy (3-75) in this region. The general solution is for the case $4a < -[1 + 4\ell(\ell + 1)]$,

$$f_\ell(r) = Ar^{-\frac{1}{2}}\cos[\gamma \log r + B],\tag{3-79}$$

where $\gamma^2 = (-a - l(l+1) - 1/4)$ and A and B are constants. This function has an infinite number of nodes and as the number of nodes in the wave function at zero energy is equal to the number of bound states (Landau and Lifshitz, 1958), it follows that any potential which becomes equal to a/r^2 for r beyond a certain value r_0 supports an infinite number of bound states if a is sufficiently negative. It will be seen later that this observation has an important application in the theory of electron scattering by atoms with degenerate energy levels.

Effective range formulae

In the important case of a potential varying like an inverse fourth power for large r,

$$U(r) = -\left(\frac{a}{r^4}\right),$$

effective range expansions have been obtained by O'Malley et al. (1961). It was shown that the Schrödinger equation had an exact solution in terms of Mathieu functions and the known properties of these functions were used to investigate the expansion of the phase shift about zero energy. The same results for $l = 0$ have been found by Martynenko et al. (1963) in a different way, and the general problem for potentials varying like $1/r^n$ has been considered by Levy and Keller (1963). We will be content to quote the results for the inverse fourth power potential. These are

$$\tan \delta_0 = Ak - \frac{\pi}{3}ak^2 + \frac{4}{3}aAk^3 \log k + 0(k^3) ,$$

$$\tan \delta_1 = \frac{\pi}{15} ak^2 + A_1 k^3 + 0(k^4), \qquad\qquad (3\text{-}80)$$

$$\tan \delta_l = \pi ak^2/[(2l + 3)(2l + 1)(2l - 1)] + 0(k^4), \quad l > 1.$$

The low energy form of the elastic scattering cross section is then (O'Malley, 1963)

$$\sigma = 4\pi\left[A^2 - \frac{2}{3}\pi aAk + \frac{8}{3}aA^2k^2 \log k + Bk^2 + \dots\right], (3\text{-}81)$$

where B is a parameter depending on the effective range.

An interesting example of the use of these equations

occurs in the work of O'Malley (1963), who determined the scattering length for electron scattering by the rare gases from the cross section measurements of Ramsauer and Kollath (1929, 1932). The polarizabilities a of the gases concerned, He, Ne, Ar, Kr and Xe are 1.36, 2.65, 11.0, 16.6 and 27.0 (in atomic units), respectively. The s wave scattering length A, can then be determined if δ_0 is known for a certain value of k close to threshold. When A is positive we have

$$\tan \delta_0 = |A|k - \frac{\pi}{3}ak^2 \qquad (3-82)$$

and δ_0 vanishes when $k = 3|A|/(\pi a)$, giving rise to a dip in the cross section, provided that scattering in the higher partial waves is small. This is known as the Ramsauer-Townsend effect and it is observed in Ar, Kr and Xe at energies 0.37 ev, 0.60 ev and 0.65 ev above threshold respectively. From these figures the computed scattering lengths are Ar(+1.9), Kr(+3.7) and Xe(+6.2) in atomic units. The phase shift δ_1 also vanishes at an energy between 1 and 1.5 ev for all these gases, except helium, and this allows a similar calculation of A_1. If the zero occurs at $k = k_1$, then

$$A_1 = -\frac{\pi a}{15k_1}.$$

The results are Ne(-1.66), Ar(-8.0), Kr(-12.8) and Xe(-23.2). More accurate results for the $\ell = 0$ scattering length are obtained by detailed fitting of the cross section as a function of energy. These results are shown in Table 3-1.

Table 3-1

Scattering lengths $(\ell = 0)$ for electron scattering by the rare gases

Gas	He	Ne	Ar	Kr	Xe
Scattering length (atomic units)	-1.19	-0.24	+1.70	+3.7	+6.5

The values shown in Table 3-1 agree rather well with similar calculations by Martynenko et al. (1963) for Ar, Kr and Xe and by Biberman and Norman (1964) for Ne and Ar.

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Chapter 4

GENERAL THEORY OF COLLISIONS

4-1 WAVE FUNCTIONS AND BOUNDARY CONDITIONS FOR MANY CHANNEL SCATTERING

Reaction channels

The theory so far developed is suitable for the description of scattering in which neither the target nor the projectile has internal structure. The theory must be extended to more realistic situations so that we can treat the scattering of electrons by atoms or atoms by atoms where both excitation and rearrangement are possible. For example, in proton-helium collisions, the reactions

$$p + He(1s^2) \rightarrow p + He(1s^2), \qquad (a)$$
$$p + He(1s^2) \rightarrow p + He(1s,2s), \qquad (b) \qquad (4-1)$$
$$p + He(1s^2) \rightarrow H(1s) + He^+(1s), \qquad (c)$$
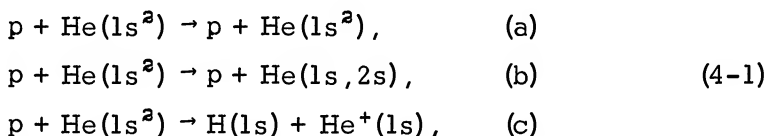
are just three of the many possibilities. The first is elastic scattering, the second excitation and the third, in which an electron is transferred between the colliding systems, is known as charge exchange. Each different incident or final state defines a reaction channel. The three channels concerned in the reactions 4-1 are then

$$p + He(1s^2), \qquad (a)$$
$$p + He(1s,2s), \qquad (b) \qquad (4-2)$$
$$H(1s) + He^+(1s) \qquad (c)$$

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The total energy E may not always be sufficient to excite a particular channel and in this case the channel is said to be closed. For example in the reactions

$$e^- + H(1s) \rightarrow e^- + H(1s), \qquad (a)$$
$$\rightarrow e^- + H(2s), \qquad (b) \qquad (4\text{-}3)$$
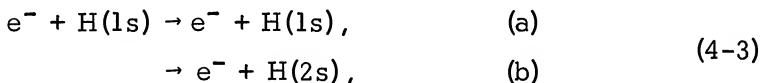
elastic scattering (a) is possible at all energies exceeding the ground state energy of hydrogen, while (b) is only possible when the total energy of the system exceeds -3.4 ev. Below this energy channel (a) is 'open' and (b) is 'closed'; above this energy both channels are open. Not all reactions are possible between a given set of particles, even if sufficient energy is available, because the appropriate quantum numbers (angular momentum, parity and so on) must be conserved.

The different reactions are of two types. Those for which the target and projectile contain the same particles before and after the collision as in (4-1a) and (4-1b), and those for which particles are transferred between the colliding systems during the reaction, as in (4-1c). We shall call the first type a direct collision and the second a rearrangement collision. The channels will be labelled $\alpha_m, \beta_n \ldots$ where $\alpha, \beta \ldots$ stand for the different arrangements, and the subscripts denote the different channels within a given arrangement. For example reactions (4-1a) and (4-1b) belong to the same arrangement and might be labelled α_1, α_2, while (4-1c) belongs to a different arrangement and might be labelled β_1.

The unperturbed state vectors describing a particular channel γ_m will be denoted by $|\varphi_{\gamma_m}\rangle$ and, to save an elaborate notation, γ_m includes all the information necessary to define the state concerned. Only the case in which each channel contains two atoms will be considered explicitly, although the formalism is quite general.

At a given energy E, the complete state vector of the system satisfies the Schrödinger equation

$$(H - E)|\Psi\rangle = 0. \qquad (4\text{-}4)$$

The Hamiltonian H can be split in different ways corresponding to each arrangement as

$$H = H_\alpha + V_\alpha$$
$$= H_\beta + V_\beta \qquad\qquad (4\text{-}5)$$
$$\vdots$$
$$= H_\gamma + V_\gamma$$
$$\vdots$$

where $V_\alpha, V_\beta, V_\gamma$ are the interaction potentials acting between the colliding atoms in arrangements α, β, γ. The unperturbed state vectors $|\varphi_{\gamma_m}\rangle$ then satisfy the Schrödinger equations

$$(H_\gamma - E)|\varphi_{\gamma_m}(E)\rangle = 0. \qquad\qquad (4\text{-}6)$$

For a given configuration γ, the unperturbed state vectors are orthogonal and form a complete set. The state vectors for different configurations are not necessarily orthogonal, and as we shall see this gives rise to some difficulties in the theory of rearrangement collisions, however if wave packets are formed, the overlap between the colliding packets will vanish as $t \to \pm\infty$, even in a rearrangement collision, and this is all that is necessary for the establishment of the theory.

As an example of the form of an unperturbed wave function[1] in the position representation, we can consider the $\{H(1s) + He^+(1s)\}$ system (4-2c). The unperturbed wave function is φ_{γ_m} which has the form

$$\varphi_{\gamma_m} = N_{\gamma_m} e^{i\mathbf{k}_{\gamma_m} \cdot \mathbf{r}} X_{\gamma_m}(\mathbf{x}), \qquad\qquad (4\text{-}7)$$

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[1] Except where mentioned, the center of mass of the system of particles will always be taken as the origin of the coordinate system. This implies that the sum of the momenta of the colliding particles with respect to this origin is zero. If a transformation to a different coordinate system is made, we would pick up an extra factor in the wave function of $\exp(i\mathbf{p} \cdot \mathbf{R})$, describing the motion of the center of mass of the system, where $\mathbf{R}$ is the position of the center of mass and $\mathbf{p}$ the total momentum.

where X_{γ_m} is the product of the ground state wave functions of hydrogen and the helium ion, and N_{γ_m} is a normalization constant. The center of mass system is employed and r is the vector joining the center of masses of the hydrogen atom and helium ion and x stands collectively for the internal coordinates of the atoms. The total energy E can be expressed as

$$E_{\gamma_m} = \epsilon_{\gamma_m} + \frac{\hbar^2}{2\mu_\gamma} k^2_{\gamma_m}, \qquad (4\text{-}8)$$

where ϵ_{γ_m} is the sum of the binding energies of the colliding atoms and μ_γ is the reduced mass.

Integral equations

State vectors $|\psi_a^+\rangle$, satisfying the Schrödinger equation (4-4), can be defined that correspond to the physical situation in which there is an incident wave in channel a only[2], with outgoing waves in all channels. Following the discussion of potential scattering in Chapter 1, we expect $|\psi_a^+\rangle$ to be expressible as $\lim_{\epsilon \to 0} |\psi_a(E + i\epsilon)\rangle$, where

$$|\psi_a(E + i\epsilon)\rangle = |\varphi_a(E)\rangle + \frac{1}{E + i\epsilon - H} V_a |\psi_a(E + i\epsilon)\rangle.$$

$$(4\text{-}9)$$

The first term on the right hand side represents the incident wave, and the second contains outgoing waves only. The function $|\psi_a(E + i\epsilon)\rangle$ satisfies the equation

$$(H - E - i\epsilon)|\psi_a(E + i\epsilon)\rangle = -i\epsilon|\varphi_a(E)\rangle. \qquad (4\text{-}10a)$$

The source term on the right hand side of this equation serves to render the solution unique, and we notice that

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[2] Here and elsewhere, we shall denote a channel by $a, \beta, \ldots$ instead of $a_m, \beta_n, \ldots$ unless we particularly wish to distinguish between rearrangements and excitations.

$|\psi_a(E + i\epsilon)\rangle \rightarrow |\varphi_a(E)\rangle$ as $V_a \rightarrow 0$. In the limit $\epsilon \rightarrow 0$, $|\psi_a(E + i\epsilon)\rangle$ reduces to $|\psi_a(E)\rangle$ which satisfies the usual equation (4-4).

The verification that $|\psi_a(E + i\epsilon)\rangle$ has the required boundary conditions, can proceed exactly according to the discussion in Section 1-6, in which wave packets were constructed from the time independent solutions. In this way it can be shown that the wave packet

$$|\Psi_a^+(t)\rangle = \int \rho(E'' - E)|\psi_a(E'' + i\epsilon)\rangle \exp(-iE''t/\hbar)dE'',$$

coincides with the incident wave packet,

$$|\Phi_a(t)\rangle = \int \rho(E'' - E)|\varphi_a(E'')\rangle \exp(-iE''t/\hbar)dE'',$$

at times in the remote past, $t \rightarrow -\infty$.

Just as in Chapter 1, we can also construct a solution $|\psi_a(E - i\epsilon)\rangle$, which contains an incident wave in channel a and ingoing waves in all channels. The function $|\psi_a(E - i\epsilon)\rangle$ satisfies the equation

$$(H - E + i\epsilon)|\psi_a(E - i\epsilon)\rangle = +i\epsilon|\varphi_a(E)\rangle, \qquad (4\text{-}10b)$$

and in this case, when wave packets are constructed, $|\Psi_a^-(t)\rangle$ is a solution that coincides with the unperturbed packet $|\varphi_a(E)\rangle$ at times in the distant future $t \rightarrow +\infty$.

We shall need time dependent wave functions when we come to calculate transition rates from the S-matrix, but rather than construct wave packets, we shall indicate the finite duration of the wave train by writing

$$|\Psi_a^\pm(t)\rangle = |\varphi_a(E)\rangle e^{-iEt/\hbar} +$$

$$+ \frac{1}{E \pm i\epsilon - H_a} V_a |\psi_a(E \pm i\epsilon)\rangle e^{-i(E \pm i\epsilon)t/\hbar}.$$

$$(4\text{-}11)$$

The factor $\exp(\pm\epsilon t/\hbar)$, in the second term, ensures that $|\Psi_a^+(t)\rangle$ converges smoothly to $|\varphi_a(E)\rangle \exp(-iEt/\hbar)$ as $t \rightarrow -\infty$, and that $|\Psi_a^-(t)\rangle$ also converges smoothly to $|\varphi_a(E)\rangle \exp(-iEt/\hbar)$,

but this time as $t \to +\infty$.

The operators $(E \pm i\epsilon - H_a)^{-1}$ are the resolvents or Green's operators appropriate to the division of the total Hamiltonian in channel a, in which we write H as $H = H_a + V_a$. Each division of the Hamiltonian gives rise to a Green's operator for the corresponding channel. We shall denote the Green's operator corresponding to channel γ as $G_\gamma^\pm(E)$, where

$$G_\gamma^\pm(E) = \lim_{\epsilon \to 0^+} G_\gamma(E \pm i\epsilon),$$

and

$$G_\gamma(E \pm i\epsilon) = \left(\frac{1}{E \pm i\epsilon - H_\gamma} \right) \qquad (4\text{-}12)$$

The Green's operator corresponding to the complete Hamiltonian H is defined in a similar way as $G^\pm(E)$, where

$$G^\pm(E) = \lim_{\epsilon \to 0^+} G(E \pm i\epsilon),$$

and

$$G(E \pm i\epsilon) = \left(\frac{1}{E \pm i\epsilon - H} \right). \qquad (4\text{-}13)$$

The integral equation (4-9) for $|\psi_a\rangle$ is written in terms of $G_a = (E + i\epsilon - H_a)^{-1}$, which is the resolvent appropriate to the division of the Hamiltonian in the incident channel, $H = H_a + V_a$. From equations (4-10a,b) we can obtain an integral equation based on the Green's operator for a channel γ, which is not the incident channel. After a little algebra we find

$$|\psi_a(E \pm i\epsilon)\rangle = G_\gamma(E \pm i\epsilon) \left\{ \pm i\epsilon |\varphi_a(E)\rangle + V_\gamma |\psi_a(E \pm i\epsilon)\rangle \right\}$$
$$(\gamma \neq a), \qquad (4\text{-}14)$$

and this is valid for all γ except $\gamma = a$, for which (4-9) is obtained. It is important in this equation not to omit the term in $i\epsilon |\varphi_a\rangle$, because in that case the equation becomes homogeneous in $|\psi_a\rangle$ and the solution is no longer unique.

It is also useful to find expressions for $|\psi_a\rangle$ in terms of the Green's operators $G^\pm(E)$ given by (4-13). Starting from equations (4-10a,b), it is straightforward to show that

$$|\psi_\alpha(E \pm i\epsilon)\rangle = \pm i\epsilon G(E \pm i\epsilon)|\varphi_\alpha(E)\rangle$$

$$= |\varphi_\alpha(E)\rangle + G(E \pm i\epsilon)V_\alpha|\varphi_\alpha(E)\rangle. \qquad (4-15)$$

4-2   THE SCATTERING MATRIX AND CROSS SECTIONS

The probability $P_{\beta\alpha}$ of finding the system in a final unperturbed state β after scattering from an initial unperturbed state α, will be written as

$$P_{\beta\alpha} = |S_{\beta\alpha}|^2, \qquad (4-16)$$

where the probability amplitudes $S_{\beta\alpha}$ form the elements of the scattering or **S**-matrix. It is convenient also to introduce a scattering operator **S**, which is defined so that

$$S_{\beta\alpha} = \langle\varphi_\beta(E_\beta)|S|\varphi_\alpha(E_\alpha)\rangle. \qquad (4-17)$$

The probability that <u>some</u> final state is reached must be unity, and it follows that

$$\sum_\beta P_{\beta\alpha} = 1. \qquad (4-18)$$

The state vector $|\psi_\alpha^+\rangle$ describes a state which evolved from the unperturbed state $|\varphi_\alpha\rangle$ at $t = -\infty$, and similarly $|\psi_\beta^-\rangle$ is the state vector corresponding to the system being in the unperturbed state $|\varphi_\beta\rangle$ as $t \to +\infty$. The probability amplitude for finding the state β in the state α is $\langle\psi_\beta^-|\psi_\alpha^+\rangle$ and this is to be identified with $S_{\beta\alpha}$,

$$S_{\beta\alpha} = \langle\psi_\beta^-(E_\beta)|\psi_\alpha^+(E_\alpha)\rangle. \qquad (4-19)$$

In the center of mass system of coordinates that we are using, the sum of the momenta of the colliding particles is zero. If we had worked in an arbitrary system, each wave function would contain as a factor a term representing the motion of the center of mass of the system. In an exact treatment this term would be a localized wave packet, but for our purpose it is sufficient to use a plane wave, confined within a box of volume V. If $\mathbf{p}_\alpha$ is the total momentum of the system

and $\mathbf{R}$ the position of the centre of mass, this plane wave, suitably normalized, is $V^{-\frac{1}{2}}\exp(i\mathbf{p}_a \cdot \mathbf{R})$. Each matrix element such as $S_{\beta a}$, will contain as a factor the integral

$$V^{-1}\int_V d\mathbf{R}\,\exp\{i\mathbf{p}_a \cdot \mathbf{R} - i\mathbf{p}_\beta \cdot \mathbf{R}\} = \delta_{\mathbf{p}_a \mathbf{p}_\beta},$$

which demonstrates that the operator $\mathbf{S}$ only causes transitions that conserve the total momentum of the system. By considering the evolution in time of the wave function, we shall later demonstrate in a similar way, that $\mathbf{S}$ only gives rise to transitions that conserve the total energy of the system.

The set of states $|\psi_a^+\rangle$, together with any bound states $|\chi_i\rangle$, of the system are complete. The states $|\psi_a^-\rangle$ (together with the bound states) also form a complete set. In view of this we can write the following formal normalization and closure conditions

$$\langle\psi_a^+|\psi_\beta^+\rangle = \langle\psi_a^-|\psi_\beta^-\rangle = \delta_{a\beta}, \tag{4-20a}$$

$$\langle\chi_i|\chi_j\rangle = \delta_{ij}, \quad \langle\psi_a^\pm|\chi_i\rangle = 0, \tag{4-20b}$$

$$\sum_a|\psi_a^+\rangle\langle\psi_a^+| + \sum_i|\chi_i\rangle\langle\chi_i| = \sum_a|\psi_a^-\rangle\langle\psi_a^-| + \sum_i|\chi_i\rangle\langle\chi_i| = 1. \tag{4-20c}$$

Using these results the $\mathbf{S}$ matrix is easily shown to be unitary[3]

$$(\mathbf{S}^\dagger\mathbf{S})_{\beta a} = \sum_\gamma S_{\beta\gamma}^\dagger S_{\gamma a} = \sum_\gamma \langle\psi_\beta^+|\psi_\gamma^-\rangle\langle\psi_\gamma^-|\psi_a^+\rangle$$

$$= \langle\psi_\beta^+|\psi_a^+\rangle = \delta_{\beta a}.$$

Similarly we have that $(\mathbf{S}\mathbf{S}^\dagger)_{\beta a} = \delta_{\beta a}$.

It should be noticed that the existence of bound states does not alter this relation, as the bound states are orthogonal to both the $|\psi_\gamma^+\rangle$ and the $|\psi_\gamma^-\rangle$. The unitarity of $\mathbf{S}$ expresses the conservation of probability given by equation (4-18). In

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[3] These statements are very difficult to prove rigorously when rearrangement collisions are possible. A proof of unitarity of the $\mathbf{S}$ matrix has been given by Jauch and Marchland (1966).

the normalization equations (4-20), $\delta_{\beta a}$ is purely symbolic, β and a standing for all the variables defining the state, some of which, like the energy, are continuous. In what follows, rather than normalizing to unity, as in (4-20), we shall revert to a normalization in which the unperturbed wave functions φ_{γ_m} are of the form (4-7), with $N_{\gamma_m} = 1$, so that the wave function of relative motion is a plane wave with unit amplitude. Then

$$\langle \psi_a^+(\mathbf{k}_a) | \psi_\beta^+(\mathbf{k}_\beta') \rangle = \langle \psi_a^-(\mathbf{k}_a) | \psi_\beta^-(\mathbf{k}_\beta') \rangle = \langle \varphi_a(\mathbf{k}_a) | \varphi_\beta(\mathbf{k}_\beta') \rangle$$

where

$$\langle \varphi_a(\mathbf{k}_a) | \varphi_\beta(\mathbf{k}_\beta') \rangle = (2\pi)^3 \delta_{\beta a} \delta(\mathbf{k}_a - \mathbf{k}_\beta').$$

These normalization conditions can be written in terms of the energy. From (4-8) we have

$$\langle \varphi_a(\mathbf{k}_a) | \varphi_\beta(\mathbf{k}_\beta') \rangle = (2\pi)^3 \delta_{a\beta} \delta(E_a - E_\beta') \delta(\Omega_a - \Omega_\beta') \frac{\hbar^2}{k_a \mu_a} \quad,$$

where

$$\delta(\Omega_a - \Omega_\beta') \equiv \delta(\cos \theta_a - \cos \theta_\beta') \delta(\varphi_a - \varphi_\beta'),$$

and (θ_a, φ_a) and $(\theta_\beta', \varphi_\beta')$ are the polar angles of $\mathbf{k}_a$ and $\mathbf{k}_\beta'$.

If no interaction takes place, $\mathbf{S}$ must be the unit operator, to ensure that the initial and final states are identical. It follows that the probability that the interaction causes a transaction, will be determined by a transition operator $\mathbf{T}$, where

$$\mathbf{S} = \mathbf{1} - i\mathbf{T}. \tag{4-21a}$$

The factor $(-i)$ is introduced for later convenience. The matrix elements of $\mathbf{S}$ and $\mathbf{T}$ are related by

$$S_{\beta a} = \delta_{\beta a} - i\mathcal{J}_{\beta a}, \tag{4-21b}$$

where $\mathcal{J}_{\beta a} \equiv \langle \varphi_\beta | \mathbf{T} | \varphi_a \rangle$.

In terms of $\mathbf{T}$ the unitary condition becomes

$$\mathbf{T}^\dagger \mathbf{T} = i(\mathbf{T} - \mathbf{T}^\dagger). \tag{4-21c}$$

The transition rate

In order to discuss the transition rate from an initial state α to a final state β, we must display the time dependence of the state vectors, and we can use for this purpose the functions $|\Psi_\alpha^\pm(t)\rangle$ defined by equation (4-11). The transition probability at a certain time is then determined by the **S**-matrix

$$\mathcal{S}_{\beta\alpha}(t) = \langle \Psi_\beta^-(E_\beta, t) | \Psi_\alpha^+(E_\alpha, t) \rangle.$$

If the observations are made at a time t which is long compared with $(\hbar/\epsilon)$, we see that $\langle \Psi_\beta^-(E_\beta, t) |$ can be replaced by $\langle \varphi_\beta(E_\beta) | \exp(iE_\beta t/\hbar)$, as the second term in (4-11) is exponentially decreasing with t. We then have that, for large t,

$$\mathcal{S}_{\beta\alpha}(t) = \langle \varphi_\beta(E_\beta) | \varphi_\alpha(E_\alpha) \rangle \exp\{i(E_\beta - E_\alpha)t/\hbar\} +$$

$$+ \exp\{i(E_\beta - E_\alpha - i\epsilon)t/\hbar\} \langle \varphi_\beta(E_\beta) | \frac{1}{E_\alpha + i\epsilon - H_\alpha} V_\alpha | \psi_\alpha(E_\alpha + i\epsilon) \rangle.$$

At this point, we shall assume that the channels β and α belong to the same arrangement, so that $H_\alpha = H_\beta$; $V_\alpha = V_\beta$, and hence

$$(E_\alpha + i\epsilon - H_\alpha)\varphi_\beta(E_\beta) = (E_\alpha + i\epsilon - E_\beta)\varphi_\beta(E_\beta).$$

The second term in $\mathcal{S}_{\beta\alpha}(t)$ represents the transitions caused by the interaction, and from (4-21b) we have that

$$-i\mathcal{T}_{\beta\alpha}(t) = \left[\frac{\exp\{i(E_\beta - E_\alpha - i\epsilon)t/\hbar\}}{(E_\alpha + i\epsilon - E_\beta)} \right] T_{\beta\alpha},$$

where $T_{\beta\alpha}$ is independent of time and is defined as

$$T_{\beta\alpha} = \langle \varphi_\beta(E_\beta) | V_\beta | \psi_\alpha(E_\alpha + i\epsilon) \rangle. \qquad (4\text{-}22a)$$

Taking the limit in which $t \to +\infty$, we have, using footnote 4 on page 31 that

$$\lim_{t\to\infty} \frac{\exp\{i(E_\beta - E_\alpha)t/\hbar\}}{(E_\alpha + i\epsilon - E_\beta)} = -2\pi i\delta(E_\beta - E_\alpha).$$

From which, we see that

$$\lim_{\epsilon \to 0} \lim_{t \to \infty} \mathfrak{J}_{\beta a}(t) = 2\pi\delta(E_\beta - E_a)T_{\beta a}(E_a). \qquad (4-22b)$$

This demonstrates that transitions only occur between states of the same energy. In terms of the time independent **S**-matrix defined by equations (4-19) and (4-21b) we can write

$$S_{\beta a} = \delta_{\beta a} - 2\pi i \delta(E_\beta - E_a)T_{\beta a}(E_a). \qquad (4-23)$$

This relation can be proved for rearrangement collisions as well as for direct collisions, and we shall show this explicitly below in the argument leading from (4-33) to (4-35).

The transition rate from the state a to the state β, $W_{\beta a}$ is determined by the equation

$$W_{\beta a} = \lim_{\epsilon \to 0} \frac{\partial}{\partial t} | \mathfrak{J}_{\beta a}(t)|^2.$$

From the expression (4-22a) we see that

$$W_{\beta a} = \lim_{\epsilon \to 0} \left[\frac{\epsilon \exp(2\epsilon t/\hbar)}{(E_a - E_\beta)^2 + \epsilon^2} \right] \frac{2}{\hbar} |T_{\beta a}|^2.$$

On taking the limit $\epsilon \to 0$, and using the relation

$$\lim_{\epsilon \to 0} \left[\frac{\epsilon}{(E_a - E_\beta)^2 + \epsilon^2} \right] = \pi\delta(E_\beta - E_a),$$

the transition rate is seen to be independent of time and to be given by the expression:—

$$W_{\beta a} = \delta(E_a - E_\beta) \frac{2\pi}{\hbar} |T_{\beta a}|^2. \qquad (4-24)$$

The transition rate vanishes unless energy is conserved, as we would expect.

The cross-section $\sigma_{\beta a}$, for the transition $a \to \beta$, is

$$\sigma_{\beta a} = \frac{1}{F_a} \Sigma' W_{\beta a}, \qquad (4-25)$$

where the sum is over the group of final states observed in the experiment, and F_a is the incident flux in channel a,

If we normalize the incident wave function so that the relative motion of the colliding particles is described by a plane wave of unit amplitude ($N_a = 1$ in 4-7) then the incident flux is

$$F_a = \frac{\hbar k_a}{\mu_a} \,.$$

For a two body final state β with center of mass momentum $\hbar k_\beta$, the total cross section is

$$\sigma_{\beta a} = \frac{2\pi}{F_a \hbar} \int \frac{d\mathbf{k}_\beta}{(2\pi)^3} \, \delta(E_a - E_\beta) |T_{\beta a}|^2 \,.$$

The $(2\pi)^3$ factor is consistent with the closure relations satisfied by the state vectors $|\varphi_\beta\rangle$, and

$$\Sigma' \to \left(\frac{1}{2\pi}\right)^3 \int d\mathbf{k}_\beta \,.$$

Using (4-8) the integration over $|\mathbf{k}_\beta|$ can be performed and $\sigma_{\beta a}$ reduces to

$$\sigma_{\beta a} = \frac{\mu_a \mu_\beta}{4\pi^2 \hbar^4} \, \frac{k_\beta}{k_a} \int d\Omega |T_{\beta a}|^2 \,, \tag{4-26}$$

where $d\Omega$ is an element of solid angle in the direction of scattering $(\theta_\beta, \varphi_\beta)$ and where

$$k_\beta^2 = \frac{\mu_\beta}{\mu_a} k_a^2 + \frac{2\mu_\beta}{\hbar^2} (\epsilon_a - \epsilon_\beta) \,. \tag{4-27}$$

It is usual to define a scattering amplitude $f_{\beta a}(\theta)$ such that

$$\frac{d\sigma_{\beta a}}{d\Omega} = \frac{v_\beta}{v_a} |f_{\beta a}(\theta)|^2 \,, \tag{4-28}$$

where v_β and v_a are the relative velocities in the states a, β

$$v_\beta = \hbar k_\beta / \mu_\beta \,, \quad v_a = \hbar k_a / \mu_a \,.$$

Then

$$f_{\beta a}(\theta) = -\left(\frac{\mu_\beta}{2\pi\hbar^2}\right)T_{\beta a} . \tag{4-29}$$

The sign is chosen to agree with that adopted for the scattering amplitude in potential scattering.

The optical theorem

The optical theorem, proved in Chapter 1 for scattering by a central potential, is always valid, as we shall now demonstrate. From (4-21c), the unitarity condition is

$$\sum_\beta T^*_{\beta a} T_{\beta a} = -2\,\mathrm{Im}\,T_{aa}. \tag{4-30}$$

As **T** only connects states of the same energy, the sum over β is a sum over all states energetically accessible from the state a. On extracting the energy conserving delta function, with the help of equation (4-22b), equation (4-30) becomes

$$\sum_\beta (2\pi)\,\delta(E_a - E_\beta)\,|T_{\beta a}|^2 = -2\,\mathrm{Im}\,T_{aa}. \tag{4-31}$$

From (4-24) and (4-25), the left hand side of this equation is seen to be related to the total cross section for scattering from state a. We have

$$\hbar F_a \left(\sum_\beta \sigma_{\beta a}\right) = -2\,\mathrm{Im}\,T_{aa}.$$

On the right hand side T_{aa} is the amplitude for a transition in which the final and initial states are identical. If a is a two particle state (the state β can contain any number of particles), the flux factor F_a is $(\hbar k_a/\mu_a)$, and we find

$$\sigma = \sum_\beta \sigma_{\beta a} = -\left(\frac{2\,\mathrm{Im}\,T_{aa}}{\hbar F_a}\right) = \left(\frac{4\pi}{k_a}\right)\mathrm{Im}\,f_{aa}(\theta_a = 0). \tag{4-32}$$

This is the general form of the optical theorem. It should be emphasized that $\mathrm{Im}\,f_{aa}(\theta_a = 0)$, the imaginary part of the forward elastic scattering amplitude, refers to scattering without change in spin or other variable.

Calculation of $S_{\beta a}$ and $T_{\beta a}$

We will now rederive equations (4-23) and (4-22a), in a form applicable to both direct and rearrangement collisions. Substituting $|\psi_\beta^-\rangle$, as given by (4-15), into (4-19), we obtain

$$S_{\beta a} = \langle\varphi_\beta | 1 + V_\beta G(E_\beta + i\epsilon) | \psi_a^+\rangle, \qquad (4\text{-}33)$$

where we have used the result

$$G^\dagger(E_\beta - i\epsilon) = G(E_\beta + i\epsilon).$$

Writing (4-14) in the form

$$(H_\beta - E_a - i\epsilon)|\psi_a(E_a + i\epsilon)\rangle = -i\epsilon|\varphi_a(E_a)\rangle - V_\beta|\psi_a(E_a + i\epsilon)\rangle,$$

the first term in (4-33) can be expressed as

$$\langle\varphi_\beta|\psi_a^+\rangle = -\frac{i\epsilon}{E_\beta - E_a - i\epsilon}\langle\varphi_\beta|\varphi_a\rangle - \frac{1}{E_\beta - E_a - i\epsilon}\langle\varphi_\beta|V_\beta|\psi_a(E_a + i\epsilon)\rangle.$$

$$(4\text{-}34)$$

Taking the limit $\epsilon \to 0^+$ we find from (4-33) and (4-34)

$$S_{\beta a} = \delta_{\beta a} - 2\pi i\delta(E_a - E_\beta)\langle\varphi_\beta|V_\beta|\psi_a^+\rangle, \qquad (4\text{-}35)$$

where we have used the relation

$$\underset{\epsilon\to 0}{lt}\left\{\frac{1}{E_a - E_\beta + i\epsilon} - \frac{1}{E_a - E_\beta - i\epsilon}\right\} = \underset{\epsilon\to 0}{lt}\frac{-2i\epsilon}{(E_a - E_\beta)^2 + \epsilon^2}$$

$$= -2\pi i\delta(E_a - E_\beta).$$

The derivation of (4-35) is correct both for direct collisions and for those involving rearrangement. Consistently with equation (4-23), the definition of $T_{\beta a}$ is in all cases taken to to be

$$T_{\beta a}(E) = \langle\varphi_\beta|V_\beta|\psi_a^+\rangle, \qquad (4\text{-}36)$$

where both φ_β and ψ_a^+ have the same energy E; that is, $T_{\beta a}$ is 'on the energy shell'.

The Born expansion and the Born approximation

From (4-15) and (4-36), the transition matrix can be written in terms of $G^+(E)$

$$T_{\beta a}(E) = \langle \varphi_\beta | T | \varphi_a \rangle = \langle \varphi_\beta | V_\beta (1 + G^+ V_a) | \varphi_a \rangle. \quad (4\text{-}37)$$

By expanding G^+ in terms of one of the Green's functions G_γ^+, various Born expansions can be obtained. To do this, we find an equation for G^+ in terms of G_γ^+, by operating from the left on both sides of (4-13) with $(H_\gamma - E - i\epsilon)$, giving

$$(H_\gamma - E - i\epsilon)G^+ = -1 - V_\gamma G^+,$$

or

$$G^+ = \frac{1}{H_\gamma - E - i\epsilon} (-1 - V_\gamma G^+) = G_\gamma (1 + V_\gamma G^+). \quad (4\text{-}38)$$

This equation can be iterated by substituting for G^+ on the right hand side, obtaining

$$G^+ = G_\gamma + G_\gamma V_\gamma G_\gamma + G_\gamma V_\gamma G_\gamma V_\gamma G^+.$$

By repeating this procedure, we find an infinite series for G^+ :—

$$G^+ = G_\gamma^+ + G_\gamma^+ V_\gamma G_\gamma^+ + G_\gamma^+ V_\gamma G_\gamma^+ V_\gamma G_\gamma^+ + \dots. \quad (4\text{-}39)$$

By using such a series expansion, it is clear that many different Born expansions for the transition matrix can be found corresponding to different choices of G_γ. For elastic scattering or excitation it is natural to choose $\gamma = a$, where a is the incident state, and for such collisions $V_a = V_\beta$ so that

$$T_{\beta a}(E) = \langle \varphi_\beta | V_a + V_a G_a V_a + \dots | \varphi_a \rangle. \quad (4\text{-}40)$$

The first Born approximation consists in retaining the first term of this expansion; if two terms are retained, we have the second Born approximation and so on. The conditions ensuring the accuracy of the first Born approximation,

$$T_{\beta a}^B = \langle \varphi_\beta | V_a | \varphi_a \rangle, \quad (4\text{-}41)$$

are similar to those discussed in potential scattering. For

rearrangement collisions the position is different, and it is possible that the series do not converge at any energy. This will be discussed later.

The transition matrix in configuration space

In discussing the position representation, attention will again be confined to the case in which each channel contains just two atoms and three body collisions will not be treated explicitly. The Green's functions G_γ^+ may be expanded in terms of the eigenfunctions of the Hamiltonian H_γ. As before, let us denote the internal coordinates of the colliding atoms collectively by $\mathbf{x}$, and the vector joining the center of masses of the colliding atoms, in the arrangement γ, by $\mathbf{r}$. The eigenfunctions of H_γ are $\varphi_{\gamma_m}(\mathbf{r},\mathbf{x})$, where

$$(H_\gamma - E_{\gamma_m})\varphi_{\gamma_m}(\mathbf{r},\mathbf{x}) = 0. \tag{4-42}$$

The functions φ_{γ_m} are given by equation (4-7) and the eigenvalues E_{γ_m} by (4-8). The normalization adopted is to set $N_{\gamma_m} = 1$ in (4-7), while the products of the internal wave functions of the atoms, X_{γ_m} form a complete orthonormal set,

$$\int X_{\gamma_m}^*(\mathbf{x}) X_{\gamma_n}(\mathbf{x}) d\mathbf{x} = \delta_{nm}. \tag{4-43}$$

The Green's functions $G_\gamma^\pm$ in configuration space are then defined by

$$G_\gamma^\pm(\mathbf{x},\mathbf{r};\ \mathbf{x}',\mathbf{r}') = \langle \mathbf{x},\mathbf{r} \mid \frac{1}{E \pm i\epsilon - H_\gamma} \mid \mathbf{x}',\mathbf{r}' \rangle, \tag{4-44}$$

and on expanding in terms of the functions φ_{γ_m} we obtain

$$G_\gamma^\pm(\mathbf{x},\mathbf{r};\ \mathbf{x}',\mathbf{r}') = \sum_m \left(\frac{1}{2\pi}\right)^3 \int d\mathbf{k}_{\gamma_m}' \left(E - E_{\gamma_m}' \pm i\epsilon\right)^{-1} X_{\gamma_m}(\mathbf{x})$$

$$X_{\gamma_m}^*(\mathbf{x}') \exp\left\{i\mathbf{k}_{\gamma_m}' \cdot (\mathbf{r} - \mathbf{r}')\right\},$$

where

$$E'_{\gamma_m} \equiv \epsilon_{\gamma_m} + \frac{\hbar^2}{2\mu_\gamma}(k'_{\gamma_m})^2 .$$

We now write $G_\gamma^\pm$ in the form,

$$G_\gamma^\pm(\mathbf{x}, \mathbf{r}; \mathbf{x}', \mathbf{r}') = \sum_m \frac{2\mu_\gamma}{\hbar^2} X_{\gamma_m}(\mathbf{x}) X_{\gamma_m}^*(\mathbf{x}') \times$$

$$\times \left(\frac{1}{2\pi}\right)^3 \int d\mathbf{k}'_{\gamma_m} \frac{\exp\{i\mathbf{k}'_{\gamma_m} \cdot (\mathbf{r}-\mathbf{r}')\}}{(k_{\gamma_m}^2 - k_{\gamma_m}'^2 \pm i\epsilon)} , \quad (4\text{-}45)$$

where $k_{\gamma_m}^2$ is defined by the equation,

$$k_{\gamma_m}^2 = \frac{2\mu_\gamma}{\hbar^2}(E - \epsilon_{\gamma_m}) .$$

By referring to equation (1-125), the last factor in (4-45) is seen to be equal to the free particle Green's function $G_o^\pm$, and $G_\gamma^\pm$ can be written finally as

$$G_\gamma^\pm(\mathbf{x}, \mathbf{r}; \mathbf{x}', \mathbf{r}') = \sum_m \frac{2\mu_\gamma}{\hbar^2} X_{\gamma_m}(\mathbf{x}) X_{\gamma_m}^*(\mathbf{x}') G_o^\pm(k_{\gamma_m}; \mathbf{r}, \mathbf{r}') ,$$

$$(4\text{-}46)$$

where the free particle Green's functions are

$$G_o^\pm(k_{\gamma_m}; \mathbf{r}, \mathbf{r}') = -\frac{1}{4\pi} \frac{1}{|\mathbf{r} - \mathbf{r}'|} \exp\{\pm i k_{\gamma_m} |\mathbf{r} - \mathbf{r}'|\} .$$

We are now in a position to examine the asymptotic form of the wave function as we let r, the mutual separation of the colliding atoms in arrangement γ, become large. The integral equation for the complete wave function, when the incident state is a_n, is

$$\psi_{a_n}^+ (\mathbf{r},\mathbf{x}) = \varphi_{a_n} (\mathbf{r},\mathbf{x}) \delta_{a,\gamma} +$$

$$+ \int d\mathbf{x}' \int d\mathbf{r}' \, G_\gamma^{\pm}(\mathbf{x},\mathbf{r}; \, \mathbf{x}',\mathbf{r}') V_\gamma(\mathbf{x}',\mathbf{r}') \psi_{a_n}^+ (\mathbf{r}',\mathbf{x}').$$

Using the asymptotic form of $G_0^{\pm}$ for large r, obtained in Chapter 1, we have that

$$\psi_{a_n}^+ (\mathbf{r},\mathbf{x}) \underset{r \to \infty}{\sim} \varphi_{a_n} (\mathbf{r},\mathbf{x}) \delta_{a,\gamma} +$$

$$+ \sum_{\gamma_m} \left(-\frac{\mu_\gamma}{2\pi\hbar^2} \right) X_{\gamma_m} (\mathbf{x}) T_{\gamma_m,a_n} r^{-1} \exp \left(ik_{\gamma_m} r \right),$$

where T_{γ_m,a_n} is defined by

$$T_{\gamma_m,a_n} = \int d\mathbf{x} \int d\mathbf{r} X_{\gamma_m}^* (\mathbf{x}) e^{-i\mathbf{k}_{\gamma_m}\cdot\mathbf{r}} V_\gamma(\mathbf{x},\mathbf{r}) \psi_{a_n}^+ (\mathbf{r},\mathbf{x}).$$

$$(4\text{-}47a)$$

The amplitude of the outgoing wave in the state γ_m, is the scattering amplitude, $f_{\gamma_m,a_n}(\theta)$, connected to the cross section by (4-29),

$$f_{\gamma_m,a_n} (\theta) = -\left(\frac{\mu_\gamma}{2\pi\hbar^2} \right) T_{\gamma_m,a_n}, \qquad (4\text{-}47b)$$

and this is in agreement with the expressions that we obtained earlier.

The function $\psi_{a_n}^+ (\mathbf{r},\mathbf{x})$ contains in the channel a_n the incident plane wave φ_{a_n}, and has outgoing waves in all channels that are open at a given energy. If the number of open channels is N, we can obtain N independent solutions of the Schrödinger equation, by placing the incident wave in each of the N channels in turn. From the asymptotic form of

the N solutions the complete N × N transition matrix can be calculated using (4-47a).

4-3   THE REDUCTION OF THE S-MATRIX

No matter what the reaction, several quantities must be conserved in addition to the energy and momentum. For instance, charge is always conserved and it follows that the matrix elements of **S** connecting states of different charge must vanish, that is, **S** is diagonal in the charge. The total angular momentum is a constant of the motion and for reactions involving light atoms, the total spin and the total orbital angular momentum are conserved separately (to a high degree of approximation). The **S**-matrix can correspondingly be diagonalized in these quantities. The problem of reducing the **S**-matrix to diagonal form has been considered by Blatt and Biedenharn (1952), when each channel contains two particles. Rather than pursue this problem in full generality, one of the simpler cases will be treated.

Let us start by supposing that in each channel the total spin and total internal orbital angular momentum of each of the colliding particles is zero. The total angular momentum, **L,** of the system then coincides with the orbital angular momentum of relative motion and a representation can be found in which L^2 and L_Z are diagonal with quantum numbers ℓ and m

$$L^2 = \ell(\ell + 1)\hbar^2,$$

$$L_Z = m\hbar.$$

The eigenvectors of L^2 and L_z, describing the unperturbed state in channel a, will be labelled $|\ell,m,a\rangle$, and these may be formed by projecting the plane wave states $|\varphi_a(\mathbf{k}_a)\rangle$ on the spherical harmonics $Y_{\ell,m}(\theta_a,\varphi_a)$, where (θ_a,φ_a) are the polar angles of k_a since the spherical harmonics are the simultaneous eigenfunctions of L^2 and L_z with quantum numbers ℓ,m.

It is only necessary to consider states of the same energy so that the factor $\delta(E_a - E_\beta)$ can be omitted in the normalization, and we can write the normalization condition as

$$\langle \varphi_\alpha(\mathbf{k}_\alpha) | \varphi_\beta(\mathbf{k}_\beta) \rangle = (2\pi)^3 \delta_{\alpha\beta} \delta(\Omega_\alpha - \Omega_\beta)\left(\frac{\hbar^2}{\mu_\alpha k_\alpha}\right). \quad (4\text{-}48)$$

With this normalization, the states $|\ell, m, a\rangle$ are defined as

$$|\ell, m, a\rangle = (2\pi)^{-3/2} \sqrt{\frac{\mu_a k_a}{\hbar^2}} \int d\Omega_a Y_{\ell,m}(\theta_a, \varphi_a) |\varphi_a(\mathbf{k}_a)\rangle,$$

$$(4\text{-}49)$$

where

$$\langle \ell', m', \beta | \ell, m, a \rangle = \delta_{\ell\ell'} \delta_{mm'} \delta_{\alpha\beta}, \quad (4\text{-}50)$$

and the closure relation is

$$\sum_{\ell, m, a} |\ell, m, a\rangle\langle \ell, m, a| = \mathbf{1}.$$

Another way of expressing (4-49) is by the equation

$$\langle \varphi_a(\mathbf{k}_a) | \ell, m, \beta \rangle = \delta_{\alpha\beta} Y_{\ell,m}(\theta_a, \varphi_a)(2\pi)^{3/2} \sqrt{\frac{\hbar^2}{\mu_a k_a}} \; .$$

$$(4\text{-}51)$$

Making use of (4-49), (4-51) and the completeness relation (4-50), the transition matrix can be expanded as

$$T_{\beta\alpha}(E) = \langle \varphi_\beta(\mathbf{k}_\beta) | \mathbf{T} | \varphi_\alpha(\mathbf{k}_\alpha) \rangle$$

$$= \sum_{\ell, \ell'} \sum_{m, m'} \sum_{\gamma, \gamma'} \langle \varphi_\beta(\mathbf{k}_\beta) | \ell, m, \gamma \rangle\langle \ell, m, \gamma | \mathbf{T} | \ell', m', \gamma' \rangle\langle \ell', m', \gamma' | \varphi_\alpha(\mathbf{k}_\alpha) \rangle$$

$$(4\text{-}52)$$

As pointed out above, the transition matrix is diagonal in ℓ and m, and since the transition probability cannot depend on the orientation of the complete system, the transition matrix must be independent of m; and can be written in the form

$$\langle \ell, m, \gamma | \mathbf{T} | \ell', m', \gamma' \rangle = -\frac{1}{\pi} T_{\gamma\gamma'}^\ell \delta_{\ell\ell'} \delta_{mm'} . \quad (4\text{-}53)$$

The factor $(-1/\pi)$ is introduced so that the diagonal elements $T_{\gamma\gamma}^\ell$ have the same normalization as the transition matrix

elements T_ℓ introduced in Chapter 1.

Using (4-53), the transition matrix element (4-52) reduces to

$$T_{\beta a}(E) = -\sum_{\ell,m} T_{\beta a}^{\ell}(E) Y_{\ell,m}^{*}(\theta_\beta, \varphi_\beta) Y_{\ell,m}(\theta_a, \varphi_a) \frac{8\pi^2 \hbar^2}{\sqrt{\mu_a \mu_\beta k_a k_\beta}}$$

$$(4-54a)$$

$$= -\sum_{\ell} T_{\beta a}^{\ell}(E)(2\pi)(2\ell+1) P_\ell(\cos\theta) \frac{\hbar^2}{\sqrt{\mu_a \mu_\beta k_a k_\beta}} ,$$

where in the second line the addition theorem for the spherical harmonics has been used. The angle of scattering θ is the angle between the vectors $\mathbf{k}_a$ and $\mathbf{k}_\beta$.

The diagonal elements of $T_{\beta a}^{\ell}(E)$ describe elastic scattering and, as in Chapter 1, these elements may be written in terms of a real phase shift δ_{β_ℓ} and an inelasticity parameter η_{β_ℓ}. Taking into account the relation between $S_{\beta a}$ and $T_{\beta a}$, we find that

$$T_{\beta\beta}^{\ell}(E) = \frac{1}{2i}\left(S_{\beta\beta}^{\ell} - 1\right),$$

$$(4-54b)$$

where

$$S_{\beta\beta}^{\ell} = \eta_{\beta_\ell} \exp\left(2i\delta_{\beta_\ell}\right).$$

$$(4-54c)$$

The partial cross sections of order ℓ are (using 4-54 in 4-56)

$$\sigma_{\beta a}(\ell) = \frac{4\pi(2\ell+1)}{k_a^2} \left|T_{\beta a}^{\ell}\right|^2.$$

If N channels are open at a certain energy, $T_{\beta a}^{\ell}$ is a square $N \times N$ matrix. Not all the elements are independent, because invariance under time reversal links the amplitude for the reaction $\beta \to a$ with that for $a \to \beta$ by

$$\langle \varphi_a(\mathbf{k}_a) | T | \varphi_\beta(\mathbf{k}_\beta) \rangle = \langle \varphi_\beta(-\mathbf{k}_\beta) | T | \varphi_a(-\mathbf{k}_a) \rangle. \quad (4-55)$$

In the angular momentum representation the relation is satisfied provided that

$$T^{\ell}_{\beta a} = T^{\ell}_{\beta a},$$ (4-56)

which reduces the number of independent elements of **T** or **S** to $N(N+1)/2$. As $\mathbf{S}^{\ell}$ is a unitary matrix it may be diagonalized by a real orthogonal matrix $\mathbf{R}^{\ell}$, where

$$\sum_{\beta} R^{\ell}_{\beta a} R^{\ell}_{\beta \gamma} = \delta_{a\gamma}.$$ (4-57)

If $\mathbf{R}^T$ is the transpose of **R**, we may write

$$\mathbf{S}^{\ell} = \mathbf{R}^T \bar{\mathbf{S}}^{\ell} \mathbf{R},$$ (4-58)

where $\bar{\mathbf{S}}^{\ell}$ is the diagonal matrix

$$(\bar{\mathbf{S}}^{\ell})_{a\beta} = \delta_{a\beta} \exp(2i\Delta^{\ell}_a).$$ (4-59)

The parameters Δ^{ℓ}_a are called the eigenphase shifts, and, if only one channel is open, Δ^{ℓ}_a is equal to the ordinary phase shift δ_{ℓ}. For two channel scattering the matrix elements of **R** depend on one parameter ϵ, called the mixing parameter, and **R** can be written as

$$\mathbf{R} = \begin{pmatrix} \cos\epsilon & \sin\epsilon \\ -\sin\epsilon & \cos\epsilon \end{pmatrix}.$$ (4-60)

Target with non-zero angular momentum

A more realistic case is that in which the target in channel a is in an eigenstate of orbital angular momentum of magnitude $\{\ell_a(\ell_a + 1)\hbar^2\}^{\frac{1}{2}}$ with Z component $m_a\hbar$, while we shall suppose that the scattered particles in each channel are structureless (such as electrons or protons). As we are considering the case in which the total orbital angular momentum and the total spin are separately conserved, we can reduce the transition matrix to diagonal form in **L** and **S** separately, and, to start with, we shall only deal with the orbital angular momentum.

If the orbital angular momentum of relative motion in the channel is of magnitude $\{L_a(L_a + 1)\hbar^2\}^{\frac{1}{2}}$ with Z component $M_a\hbar$ and the total orbital angular momentum of the whole system is $\{L(L + 1)\hbar^2\}^{\frac{1}{2}}$ with Z component $M\hbar$, the ordinary rules of addition of angular momenta require that

$$\left| L_a - \ell_a \right| \leq L \leq (L_a + \ell_a),$$

$$M = M_a + m_a.$$
(4-61)

The unperturbed wave functions $\varphi_a(\mathbf{k}_a)$ can be labelled by the angular momentum of the target and are of the form

$$\varphi_{a,\ell_a,m_a}(\mathbf{k}_a) = e^{i\mathbf{k}_a \cdot \mathbf{r}} X_{a,\ell_a,m_a}(\mathbf{x}),$$
(4-62)

where $X_{a,\ell_a,m_a}(\mathbf{x})$ is the target wave function. If the eigenstates of total orbital angular momentum are labelled as $|L,L_a,\ell_a,M\rangle$, with the normalization

$$\langle L',L_\beta,\ell_\beta,m' \, | \, L,L_a,\ell_a,m \rangle = \delta_{a\beta}\delta_{L'L}\delta_{L_\beta L_a}\delta_{\ell_a \ell_\beta}\delta_{m'm},$$
(4-63)

then in place of (4-49), we have

$$|L,L_a,\ell_a,M\rangle = \sum_{m_a} (2\pi)^{-3/2}\sqrt{\frac{\mu_a k_a}{\hbar^2}}\int d\Omega_a Y_{L_a M_a}(\theta_a,\varphi_a)C_{L_a \ell_a}(LM;M_a,m_a) \times$$

$$\times |\varphi_{a,\ell_a,m_a}(\mathbf{k}_a)\rangle,$$
(4-64)

where $C_{\ell_1 \ell_2}(L,M,m_1 m_2)$ is the Clebsch-Gordan coefficient relating the representation in which (L,M,ℓ_1,ℓ_2) are diagonal to that in which $(\ell_1 \ell_2 m_1 m_2)$ are diagonal. See, for example, Edmonds (1960). The expansion of $T_{\beta a}$ corresponding to (4-54a) is then easily seen to be

$$T_{\beta a}(E) = -\sum_L \sum_{L_\beta, L_a} \sum_{M_a, M_\beta} T^L_{\beta, L_\beta, \ell_\beta; a, L_a, \ell_a} Y^*_{L_\beta, M_\beta}(\theta_\beta, \varphi_\beta) Y_{L_a M_a}(\theta_a \varphi_a)$$

$$\times \sqrt{\frac{\hbar^4}{\mu_a \mu_\beta k_a k_\beta}} \; 8\pi^3 \; C_{L_a \ell_a}(L,M;M_a,m_a) C_{L_\beta \ell_\beta}(L,M;M_\beta,m_\beta)$$

(4-65)

where to satisfy rotational invariance T^L must be independent of M, M_a, m_a, M_β and m_β. If the Z axis is chosen to be in the direction of the vector $\mathbf{k}_a$ and taking $M = 0$, this expression simplifies to

$$T_{\beta a}(E) = -\sum_L \sum_{L_a, L_\beta} \sum_{M_a, M_\beta}{}' T^L_{\beta, L_\beta, \ell_\beta; a, L_a, \ell_a} \sqrt{\frac{2L+1}{4\pi}} \times$$

$$\times Y^*_{L_\beta, M_\beta}(\theta, \varphi) \, 8\pi^3 \sqrt{\frac{\hbar^4}{\mu_a \mu_\beta k_a k_\beta}} \; C_{L_\beta \ell_\beta}(L0;M_\beta,m_\beta) C_{L_a \ell_a}(L0;M_a,m_a).$$

(4-66)

The number of states connected by T^L is restricted not only by (4-61) but also by the conservation of parity. If the parity of the target is π_a in state a, and π_β in state β then L_a and L_β satisfy

$$\pi_a(-1)^{L_a} = \pi_\beta(-1)^{L_\beta}.$$

(4-67)

General expressions can be obtained from (4-66) for the differential cross section and have been given by Blatt and Biedenharn (1952), and the particular case of electron-hydrogen atom scattering has been developed by Seaton and Percival (1957). The total cross section has the simple form (making no allowance for spin)

$$\sigma_{\beta \ell_\beta, a\ell_a}(E) = \frac{4\pi}{k_a^2} \sum_L \sum_{L_\beta, L_a} \frac{(2\ell+1)}{(2\ell_a+1)} \left| T^L_{\beta, L_\beta, \ell_\beta; a, L_a, \ell_a} \right|^2.$$

(4-68)

The reduction to diagonal form of the T matrix in the spin variables of the particles can be done in the same way and will be discussed in connection with particular examples as we come to them.

The radial wave functions

It is important to determine the T matrix in the angular momentum representation in terms of radial wave functions. The case of direct collisions will be treated for simplicity, but the results will be quite general.

By expanding the complete wave functions Ψ_a^+ in a set of internal wave functions $X_\gamma(x)$, we may define a channel wave function $F_{\gamma,a}$:—

$$\Psi_a^+(r,x) = \sum_\gamma X_\gamma(x) F_{\gamma,a}^+(r), \qquad (4-69)$$

where x denotes collectively all the internal coordinates of the colliding particles and the subscript a on $F_{\gamma,a}$ denotes that the incident wave is channel a. From (4-47) the asymptotic form of $F_{\gamma,a}(r)$ is, in the open channels,

$$F_{\gamma,a}^+(r) \sim \delta_{\gamma a} e^{i k_a \cdot r} - \left(\frac{\mu_\gamma}{2\pi \hbar^2}\right) T_{\gamma a}(E) \frac{e^{i k_\gamma r}}{r}, \qquad (4-70)$$

and in the closed channels $F_{\gamma,a}(r) \to 0$ as $|r| \to \infty$

A matrix potential $V_{\gamma,\beta}(r)$ is defined by

$$V_{\gamma\beta}(r) = \int X_\gamma^*(x) V(x,r) X_\beta(x) dx, \qquad (4-71)$$

(as we are dealing with direct collisions the perturbation V does not require a channel label) and the transition matrix elements can be expressed as

$$T_{\beta a} = \sum_\gamma \int e^{-i k_\beta \cdot r} V_{\beta\gamma}(r) F_{\gamma,a}^+(r) dr. \qquad (4-72)$$

The channel wave function $F_{\gamma,a}^+(r)$ can be expanded in eigenfunctions of angular momentum. In the case where $V_{\beta\gamma}(r)$

is a function of $|\mathbf{r}|$ only, the system is axially symmetric, and the expansion is

$$F^+_{\gamma,a}(\mathbf{r}) = \sum_{\ell=0}^{\infty} A_\ell r^{-1} f_{\gamma,a}(\ell,r) P_\ell(\cos\theta), \tag{4-73}$$

where the A_ℓ are constants.

The boundary conditions satisfied by $f^+_{\gamma,a}(\ell,r)$ are then

$$f^+_{\gamma,a}(\ell,0) = 0, \tag{4-74a}$$

$$f^+_{\gamma,a}(\ell,r) \sim k_\gamma^{-1} s_\ell(k_\gamma r)\delta_{\gamma a} + \sqrt{\frac{\mu_\gamma k_\gamma}{\mu_a k_a}} \frac{e^{i(k_\gamma r - \ell\pi/2)}}{k_\gamma} T^\ell_{\gamma a}(E),$$
$$\tag{4-74b}$$

for $\gamma < N$, where N is the number of open channels and

$$f^+_{\gamma,a}(\ell,r) \to 0 \text{ as } r \to \infty, \text{ for } \gamma > N. \tag{4-74c}$$

In equation (4-74b), $T^\ell_{\gamma a}$ is related to $T_{\gamma a}$ by (4-54) and $s_\ell(x)$ is defined in Section (1-2).

The solution to the many channel scattering problem then amounts to solving the set of coupled radial Schrödinger equations

$$\frac{\hbar^2}{2\mu_\gamma}\left(\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2} + k_\gamma^2\right) f^+_{\gamma,a}(r) = \sum_{\gamma'} V_{\gamma\gamma'}(r) f^+_{\gamma',a}(r),$$
$$\tag{4-75}$$

with the boundary conditions (4-74). The indices γ and γ' run over all the channels, both open and closed. There will be N independent solutions of the coupled equations, that are conveniently defined by taking the incident wave in each open channel in turn, that is, we let a range from 1 to N.

Integral equations for the radial functions can be obtained by straightforward generalizations of the methods employed for single channel scattering and described in Chapter 1. The variational methods of Kohn, Hulthén and Schwinger are easily adapted to deal with coupled channels, and so is the determinantal method of Baker. In a more

general situation in which different arrangements are allowed, the potential matrix $V_{\gamma\beta}$ becomes a non-local integral operator, but this causes no essential difficulty.

The reaction matrix

In practice it is easier, when numerical solutions are required, to define real solutions of the coupled equations, by imposing the boundary conditions,

$$f_{\gamma,a}(\ell,0) = 0$$

$$f_{\gamma,a}(\ell,r) \sim k_\gamma^{-1} s_\ell(k_\gamma r)\delta_{a\gamma} + \sqrt{\frac{\mu_\gamma k_\gamma}{\mu_a k_a}}\, k_\gamma^{-1} c_\ell(k_\gamma r) K_{\gamma a}^\ell(E), \quad \gamma < N$$

$$(4\text{-}76)$$

$$f_{\gamma,a}(\ell,r) \to 0, \quad r \to \infty, \quad \gamma > N.$$

Comparing the solutions (4-74) and (4-76), it is seen that the reaction matrix K^ℓ is given in terms of T^ℓ by

$$K^\ell = \frac{T^\ell}{1 + iT^\ell} = \frac{1}{i}\left(\frac{S-1}{S+1}\right). \tag{4-77}$$

As S is unitary and symmetric, it follows that K is real and symmetric. An important property of the K matrix is that if it is calculated in any approximation, the S matrix elements calculated from (4-77) will be automatically unitary. The real orthogonal matrix R, that diagonalizes the S matrix, will also diagonalize T and K:—

$$K_{\beta a}^\ell = \sum_\gamma R_{\gamma\beta}\left(\tan \Delta_\gamma^\ell\right) R_{\gamma a},$$

$$T_{\beta a}^\ell = \sum_\gamma R_{\gamma a} R_{\gamma\beta}\left(\frac{e^{2i\Delta_\gamma^\ell} - 1}{2i}\right). \tag{4-78}$$

4-4   AN ILLUSTRATIVE EXAMPLE

A simple approximation,that describes the excitation of the (2s) state of hydrogen by electron impact on the ground state, is obtained if just two terms are retained in the expansion of the wave function in terms of the target eigenfunctions. For scattering in the $\ell = 0$ partial wave, we have

$$\Psi(\mathbf{r},\ \mathbf{x}) = \varphi_{1s}(\mathbf{x})r^{-1}f_1(r) + \varphi_{2s}(\mathbf{x})r^{-1}f_2(r),\qquad(4\text{-}79)$$

where φ_{1s} and φ_{2s} are the (1s) and (2s) eigenfunctions of the hydrogen atom[4]. No allowance for electron exchange has been made, and because of this the model is not very realistic, but it serves to illustrate the methods employed. The coupled radial Schrödinger equations are (in atomic units)

$$\frac{1}{2}\left(\frac{d^2}{dr^2} + k_i^2\right)f_i(r) = \sum_{j=1}^{2} V_{ij}(r)f_j(r),\qquad(4\text{-}80)$$

where

$$k_2^2 = k_1^2 + 2\left(\epsilon_{1s} - \epsilon_{2s}\right) = k_1^2 - 0.75.$$

The perturbation between the incident electron and the atom is

$$V(\mathbf{r},\mathbf{x}) = \frac{1}{|\mathbf{r} - \mathbf{x}|} - \frac{1}{r},\qquad(4\text{-}81)$$

so that the matrix potential $V_{ij}(r)$ is

$$V_{ij}(r) = \int d\mathbf{x}\,\varphi_i(\mathbf{x})\varphi_j(\mathbf{x})V(\mathbf{r},\mathbf{x}).\qquad(4\text{-}82)$$

With

$$\varphi(r) = \frac{1}{\sqrt{\pi}}\,e^{-r}$$

---

[4] The channel functions $f_i(r)$ are here only labelled by the channel to which they refer and the additional label defining the channel of the incident wave is dropped.

Table 4-1

Zero order partial cross sections for the $1s - 2s$ excitation of hydrogen by electron impact (without exchange).

Energy of incident electron	σ_{1s-2s} (units of πa_0^2)					Phase of T_{12}	
(ev)	E	DW	V_1	V_2	V_3	$\pi + \theta$	$\delta_1 + \delta_2$
11.5	0.286	--	--	--	--	3.947	--
13.5	0.204	0.198	0.110	0.164	0.189	3.643	3.66
19.4	0.102	0.127	0.055	0.081	0.094	3.060	3.08
30.4	0.045	0.058	0.027	0.035	0.040	2.636	2.61
54.0	0.0155	0.019	0.003	0.012	0.014	2.124	2.10

E: From numerical solution of equation (4-80) (Bransden and
        McKee, 1956).

DW: Distorted wave method (Erskine and Massey, 1952).

V_1, V_2, V_3: Variational method with 1, 2 and 3 polynomial
        terms in the wave functions (Bransden and McKee,
        1957).

θ, δ_1, δ_2: See text.

Table 4-2

Zero order partial cross sections for elastic scattering of electrons by the ground state of hydrogen

Energy of incident electron	σ_{1s-1s} (units of πa_0^2)	
(ev)	(a)	(b)
11.5	--	2.52
13.5	2.47	2.12
19.4	1.57	1.42
30.4	0.885	0.828
54.0	0.411	0.394

(a): From the single channel equation using the phase shifts of
        Table 1-1.

(b): From the coupled equation (4-80).

and

$$\varphi_{2s}(r) = \frac{1}{2\sqrt{(2\pi)}}\left(1 - \frac{r}{2}\right)e^{-r/2},$$

it is easily found that

$$V_{11} = -\left(1 + \frac{1}{r}\right)e^{-2r},$$

$$V_{22} = \frac{1}{2}\left(\frac{1}{4}r^2 + 5r + \frac{2}{r} - 3\right)e^{-r}, \qquad (4-83)$$

$$V_{12} = V_{21} = \frac{\sqrt{8}}{27}(6 - 3r - 8)e^{-3r/2}.$$

The partial cross sections obtained from accurate numerical solutions of equations (4-80) are shown in Tables 4-1 and 4-2. Because all the elements of the scattering matrix are calculated, the elastic cross section σ_{1s-1s} can be found as well as σ_{1s-2s}, the inelastic cross section. The same equations have been solved in variational and distorted wave approximations.

The distorted wave approximation

The distorted wave approximation is useful under conditions for which the coupling between the channels is small. If electrons are incident on the hydrogen ground state, it may be a good approximation to neglect the influence of the second channel on the elastic scattering channel, and to drop the term V_{12} in the coupled equations. We then have

$$\frac{1}{2}\left(\frac{d^2}{dr^2} + k_1^2\right)f_1(r) = V_{11}f_1(r), \qquad \text{(a)}$$

$$\frac{1}{2}\left(\frac{d^2}{dr^2} + k_2^2\right)f_2(r) = V_{22}f_2(r) + V_{21}f_1(r). \qquad \text{(b)}$$

$$(4-84)$$

The solution of equation (4-84a) with the elastic scattering boundary condition,

$$f_1(r) \sim k_1^{-1}e^{i\delta_1}\sin(k_1r + \delta_1), \qquad (4-85)$$

is easily found, and this solution may be substituted into equation (4-84b). The boundary condition satisfied by $f_2(r)$ is that outgoing waves only should appear in the second channel,

$$f_2(r) \sim \sqrt{\frac{k_2}{k_1}} \frac{e^{ik_2 r}}{k_2} T_{12}.$$

(4-86)

To construct a solution with this boundary condition, a Green's function $g_2(r, r')$ is required that satisfies

$$\left\{ \frac{1}{2}\left(\frac{d^2}{dr^2} + k_2^2 \right) - V_{22} \right\} g_2(r, r') = \frac{1}{2}\delta(r - r'),$$

in which case

$$f_2(r) = 2\int_0^\infty g_2(r, r') V_{21}(r') f_1(r') dr'.$$

(4-87)

The Green's function g_2 is given by

$$g_2(r, r') = -L(r_<)H(r_>),$$

(4-88)

where H and L are solutions of the equation

$$\left(\frac{d^2}{dr^2} + k_2^2 - 2V_{22} \right) F = 0,$$

(4-89)

with the boundary conditions

$$L(r) \sim \sin(k_2 r + \delta_2)$$

$$H(r) \sim k_2^{-1} \exp\{i(k_2 r + \delta_2)\}.$$

(4-90)

It is easy to check that (4-87) is the solution of (b) using the Wronskian relation,

$$\left(\frac{dL}{dr} H - \frac{dH}{dr} L \right) = 1.$$

(4-91)

For large r we have from (4-87) that

$$f_2(r) \sim -2k_2^{-1} e^{ik_2 r} e^{i\delta_2} \int_0^\infty L(r') V_{21}(r') f_1(r') dr',$$

(4-92)

so that

$$T_{12} = -2\sqrt{\frac{k_1}{k_2}} e^{i\delta_2} \int_0^\infty L(r) V_{21}(r) f_1(r) dr.$$

The partial cross section σ_{1s-2s} in this approximation is

included in Table 4-1. The distorted wave method predicts
that the phase of the amplitude θ, where

$$T_{12} = |T_{12}| e^{i\theta} \tag{4-93}$$

should be $(\delta_1 + \delta_2)$, where δ_1 and δ_2 are the elastic scatter-
ing phase shifts in each channel. In Table 4-1, $(\delta_1 + \delta_2)$ is
seen to be close to $(\pi + \theta)$, where θ is the exact phase. The
quoted results (from Erskine and Massey, 1952) were deter-
mined using variational rather than exact functions for $L(r)$ and
$H(r)$ so that they may misrepresent the distorted wave method
to some extent, and, except at the lowest energies, the agree-
ment between the approximate and exact results is not very
close.

A variational method

It is also interesting to see how effective the Schwinger
variational method is for an inelastic collision with a polynom-
ial wave function of the kind that was used in the single
channel example in Section 2-1. In the Schwinger method the
coupled equations are written as integral equations. In a mat-
rix notation, two solutions $\mathbf{F}^{A,B}(r)$ are defined as

$$\mathbf{F}^A(r) = \mathbf{\Phi}^A + \int_0^\infty \mathbf{G}(r,r') \mathbf{V}(r') \mathbf{F}^A(r') dr',$$

$$\mathbf{F}^B(r) = \mathbf{\Phi}^B + \int_0^\infty \mathbf{G}(r,r') \mathbf{V}(r') \mathbf{F}^B(r') dr', \tag{4-94}$$

where

$$\Phi_i^A = \delta_{i1} k_i^{-1} \sin k_i r, \qquad i = 1, 2$$

$$\Phi_i^B = \delta_{i2} k_i^{-1} \sin k_i r$$

and

$$G_{ij}(r,r') = -k_i^{-1} \sin k_i r_< \exp(ik_i r_>) \delta_{ij}.$$

The solution $\mathbf{F}^A$ has an incident plane wave in channel
1 and outgoing spherical waves in both channels and $\mathbf{F}^B$ has
an incident plane wave in channel 2, and incoming spherical
waves in both channels.

It is straightforward to show that

$$\sqrt{\frac{k_1}{k_2^3}} \, T_{12} = R = S = Y, \tag{4-95}$$

where

$$R \equiv \int_0^\infty \mathbf{\Phi}^{B\dagger}(r) \, \mathbf{V}(r) \, \mathbf{F}^A(r) dr,$$

$$S \equiv \int_0^\infty \mathbf{F}^{B\dagger}(r) \, \mathbf{V}(r) \mathbf{\Phi}^A(r) dr, \tag{4-96}$$

$$Y \equiv \int_0^\infty \int_0^\infty \mathbf{F}^{B\dagger}(r) \, \mathbf{V}(r) \left[\delta(r-r') \, \mathbf{1} - \mathbf{G}(r,r') \mathbf{V}(r')\right] \mathbf{F}^A(r') dr \, dr'.$$

The expression

$$\sqrt{\frac{k_1}{k_2^3}} \, T_{12} = RSY^{-1}$$

is stationary with respect to variations in the functions $\mathbf{F}^A$ and $\mathbf{F}^B$, if trial functions are taken of the form

$$F_i^A(r) = \sum_{n=1}^N C_{i,n}^A r^n, \quad i = 1,2, \tag{4-97}$$

$$F_i^B(r) = \sum_{n=1}^N C_{i,n}^B r^n, \quad i = 1,2.$$

The constants $C_{i,n}^{A,B}$ are found from the equations

$$\frac{\partial R}{\partial C_{i,n}^A} + \frac{\partial S}{\partial C_{i,n}^A} = \frac{\partial Y}{\partial C_{i,n}^A}, \quad i = 1,2; \quad n = 1,2,\ldots,N. \tag{4-98}$$

and similar equations for $C_{i,n}^B$. The calculated cross sections are shown in Table 4-1 for the cases with $N = 1,2,3$. The convergence is rather good in this particular case. Another variational method due to Massey and Moiseiwitch (1953) with trial functions similar to those of the one channel case given

in equation (2-15) is less successful in this example.

4-5   MANY CHANNEL SCATTERING, RESONANT STATES AND EFFECTIVE RANGE EXPANSIONS

Should one of the eigenphase shifts increase rapidly through $\pi/2$ as the energy increases, each matrix element of the **K** matrix, and also of the **T** matrix, will possess a pole which will induce a peak in the partial cross sections. As for single channel scattering, discussed earlier, this behaviour can be interpreted as being due to the formation of a metastable or resonant state. If the pole in the **T** matrix is near the real energy axis, the width of the resonance is small and the mean life of the resonant state is long compared with the natural collision time.

If E_R is an energy for which $\Delta_\delta^\ell = \pi/2$, then for E in the neighbourhood of E_R,

$$\tan \Delta_\delta^\ell = \frac{\Gamma}{E_R - E} + A(E), \qquad (4-99)$$

where

$$\Gamma^{-1} = \left. \frac{\partial \Delta_\delta^\ell}{\partial E} \right|_{E=E_R}$$

and A(E) is a slowly varying function of E. At $E = E_R$, all the elements of the reaction matrix possess a pole on the real energy axis. The corresponding pole in the transition matrix is at a complex value of E. If just one eigenphase, Δ_δ^ℓ, is resonant and if the elements $R_{\beta a}$ of the orthogonal matrix R are slowly varying with energy, then near $E = E_R$, **T** can be expressed as

$$T_{\beta a}^\ell (E) = R_{\delta a} R_{\delta \beta} \, e^{2i\varphi} \frac{\gamma}{(E_R' - E) - i\gamma/2} + \Im_{\beta a}^\ell (E), \quad (4-100)$$

where $\Im_{\beta a}^\ell (E)$ is a slowly varying background, and E_R' differs from E_R by a level shift ϵ, given in (4-102),

.

$$\mathcal{J}^{\ell}_{\beta a} = \left[R_{\delta a} R_{\delta \beta} \sin \varphi + \sum_{n \neq \delta} R_{na} R_{n\beta} e^{i \Delta^{\ell}_n} \sin \Delta^{\ell}_n \right]. \quad (4\text{-}101)$$

The width γ, the level shift $\epsilon \equiv E'_R - E_R$, and the phase φ are related to Γ and $A(E)$ by the equations,

$$\gamma(E) = \frac{2\Gamma}{1 + A^2}, \quad \epsilon = \frac{A\Gamma}{1 + A^2}, \quad e^{2i\varphi} = \frac{(1 + iA)^2}{1 + A^2}. \quad (4\text{-}102)$$

It is customary to introduce, instead of the matrix elements R_{δ_a} and R_{δ_β} partial widths γ_a and γ_β by the definitions,

$$\frac{\gamma_a}{\gamma} = \left(R_{\delta a} \right)^2 ,$$

$$(4\text{-}103)$$

$$\frac{\gamma_\beta}{\gamma} = \left(R_{\delta \beta} \right)^2 .$$

Because of the orthogonality of R, the partial widths have the property

$$\sum_a \gamma_a = \gamma, \quad (4\text{-}104)$$

where the sum extends over all the open channels. Following the discussion in Chapter 1, $\tau = (\hbar/\gamma)$ is the mean lifetime of the metastable state and the quantities $\tau_a = (\hbar/\gamma_a)$ are the lifetimes for decay into the channel a. All the partial widths must be positive.

When attempting to identify resonances from the experimental data, it is helpful to plot the trajectory of the amplitude in an Argand diagram, as the energy varies over the resonance region. A diagonal element of $\mathbf{T}^{\ell}$ can be written in the form

$$T^{\ell}_{aa}(E) = -i \left(\frac{\gamma_a}{\gamma} \right) \left(\frac{E'_R - E + i\gamma/2}{E'_R - E - i\gamma/2} \right) + \mathcal{J}^{\ell}_{aa}(E). \quad (4\text{-}105)$$

The slowly varying functions γ, γ_a and $\mathcal{J}^{\ell}_{aa}$ can usually be treated as constants over the resonances region, provided that

the width of the resonance is small, $\gamma \ll E_R'$. As E increases, T_{aa}^{ℓ} will describe a circle in the anti-clockwise direction with centre C where $0C = \mathfrak{J}_{aa}$ and of radius (γ_a / γ). This is shown in Fig. 4-1, where $0P$ represents T_{aa}^{ℓ} at an energy E.
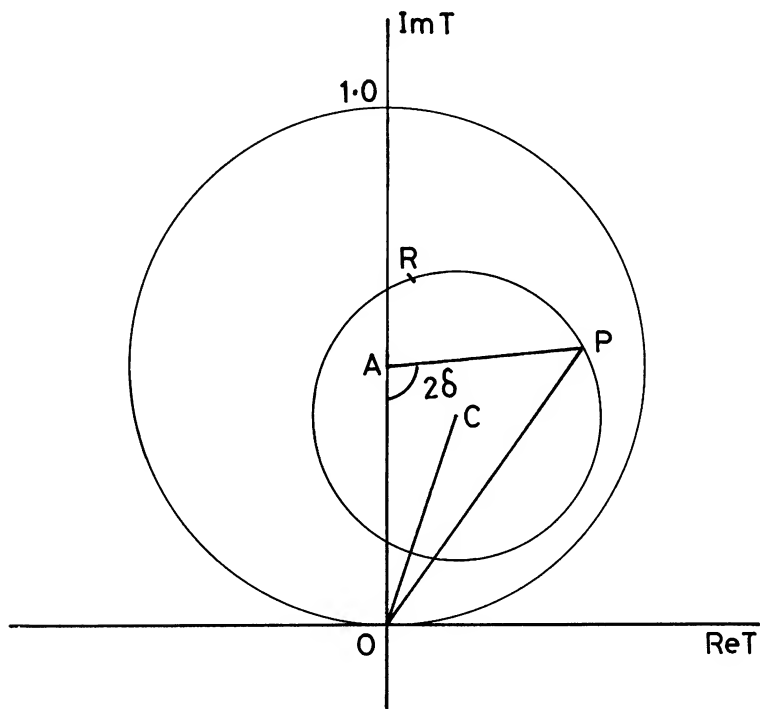
Figure 4-1   The Argand diagram representation of the scattering amplitude near a resonance.

As may be seen from the representation of T_{aa}^{ℓ} in terms of a real phase shift δ_ℓ and an inelasticity parameter η_ℓ the whole trajectory must be confined within a circle of radius 0.5, with centre at the point A with coordinates $(0, i/2)$. The angle $0AP = (2\delta_\ell)$ and $AP = (\eta_\ell / 2)$. At the resonant energy, the amplitude may be represented by some point R, which is not necessarily at the top of the circle. If the background is

small, A and C will coincide and δ_ℓ will pass through $\pi/2$ at resonance, but in general δ_ℓ may take on any value at the energy E_R, including the value zero, and in practice if the resonance is not narrow, the circle will be badly distorted.

Threshold behaviour and effective range formulae

By introducing the free particle Green's functions $g_\ell(r,r')$, equations (4-75) can be expressed as integral equations, from which it is easy, following the methods outlined in Chapter 1, to show that

$$T^\ell_{\beta a} = - \sqrt{\frac{\mu_a k_a}{\mu_\beta k_\beta}} \left(\frac{2\mu_\beta}{\hbar^2} \right) \sum_\gamma \int_0^\infty s_\ell(k_\beta r) V_{\beta\gamma}(r) f^+_{\gamma,a}(\ell,r),$$

(4-106)

where $f^+_{\gamma,a}(r)$ satisfied the boundary condition (4-74), and that

$$K^\ell_{\beta a} = - \sqrt{\frac{\mu_a k_a}{\mu_\beta k_\beta}} \left(\frac{2\mu_\beta}{\hbar^2} \right) \sum_\gamma \int_0^\infty s_\ell(k_\beta r) V_{\beta\gamma}(r) f_{\gamma,a}(\ell,r),$$

(4-107)

where $f_{\gamma,a}(r)$ now satisfies the boundary condition (4-76). In the realistic case, in which the target has structure, the angular momentum ℓ will be different in each channel. In this case the coupled equations will take the same form as (4-75) with $\ell_{\gamma'}$ the angular momentum in channel γ, replacing ℓ on the left hand side. The **T** or **K** matrices will be diagonal in the total angular momentum L, and the generalization of (4-107) is

$$K^L_{\beta a} = - \sqrt{\frac{\mu_a k_a}{\mu_\beta k_\beta}} \left(\frac{2\mu_\beta}{\hbar^2} \right) \sum_\gamma \int_0^\infty s_{\ell_\beta}(k_\beta r) V_{\beta\gamma}(r) f_{\gamma,a}(\ell_{\gamma'},r) dr.$$

(4-108)

To discuss the behaviour of $K^L_{\beta a}$ near the threshold for the reaction $\beta \to a$, as we argued in the case of single channel scattering, it is sufficient to examine the Born approximation,

which consists in replacing $f_{\gamma,a}(\ell_{\gamma'}r)$ by $\delta_{a\gamma}k_a^{-1}s_{\ell_a}(k_ar)$.

Then

$$K^L_{\beta a} = -\frac{2}{\hbar^2}\sqrt{\frac{\mu_a\mu_\beta}{k_ak_\beta}}\int_0^\infty s_{\ell_\beta}(k_\beta r)s_{\ell_a}(k_ar)V_{\beta a}(r)dr. \quad (4\text{-}109)$$

Since $k^{-\ell}s_\ell(kr)$ is an entire analytic function of k^2, it follows that $K^L_{\beta a}$ and $T^L_{\beta a}$ possess square root branch points at each threshold. If the potentials $V_{\beta a}$ are of short range, $K^L_{\beta a}$ will possess the cuts along the negative real E axis due to the potential (discussed in Chapter 1 for the single channel case), and poles on the real axis due to the bound states and resonances.[5] The branch cut at each threshold can be removed by introducing a new matrix, **M**, by the relation (Ross and Shaw, 1961)

$$\mathbf{M}(E) = \mathbf{k}^{\boldsymbol{\ell}+1/2}(\mathbf{K}^L)^{-1}\mathbf{k}^{\boldsymbol{\ell}+1/2}, \quad (4\text{-}110)$$

where $\mathbf{k}^{\boldsymbol{\ell}+1/2}$ represents a diagonal matrix with elements

$$\left(\mathbf{k}^{\boldsymbol{\ell}+1/2}\right)_{a\beta} = \delta_{a\beta}k_a^{\ell_a+1/2}. \quad (4\text{-}111)$$

The **M** matrix is analytic about each threshold and so may be expanded as a power series in E.

$$\mathbf{M}(E) = \mathbf{M}(E_0) + \frac{1}{2}\mathbf{R}_0(E - E_0) + \dots. \quad (4\text{-}112)$$

This is the analogue of the single channel effective range series and **R**$_0$ is an effective range matrix. When only a single channel is open this reduces to the usual effective range formula for $M = k^{2\ell+1}\cot\delta_\ell$.

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[5] The analytic structure of $\mathbf{T}^L$ or $\mathbf{K}^L$ can be investigated most easily by examining the Fredholm determinant associated with the whole set of coupled equations (Newton, 1961).

The branch points in the amplitude at the thresholds induce cusps into the partial cross sections, which in practice are usually not sufficiently large to be observed. There is a considerable literature on the threshold behaviour of the cross sections which may be traced from the papers of Newton (1959), Baz (1959), Fonda (1961a,b) and Delves (1958a,b).

Continuation of the reaction matrix below open thresholds

Using the analyticity of $\mathbf{M}(E)$, the reaction matrix may be continued below one or more of the open thresholds. We shall treat the case of s-waves $(\ell = 0)$, although the theory is easily generalized to any ℓ. Suppose that at a certain energy N channels are open and the N x N K matrix is defined by imposing the boundary conditions (4-76) on the radial wave functions. If the energy is now set to a value below the threshold of channel β, the highest of the N thresholds, the wave function in channel β becomes in the asymptotic region

$$f_{\beta,a}(r) \sim \delta_{\beta a} \frac{\sinh(|k_\beta|r)}{|k_\beta|} + K_{\beta a} \sqrt{\frac{\mu_\beta k_\beta}{\mu_a k_a}} \frac{\cosh(|k_\beta|r)}{|k_\beta|} .$$

$$(4-113)$$

This form may be contrasted with that applying in all the closed channels (with $\beta > N$). In that case the closed channel wave functions decrease exponentially like $\exp(-|k_\beta|r)$ and are not smooth continuations of open channel functions. The continued matrix $K_{\beta a}$ is still of dimension N x N although there are now only (N – 1) channels open. It is a Hermitian matrix but the matrix elements are no longer real.

The continuation below the thresholds can be carried out until one of the branch points associated with the potential is encountered. For example, if the interaction $V_{\alpha\beta}$ is proportional to $\exp(-\lambda r)$ then terms like $\exp\{|k|r - \lambda r\}$ occur in the wave function, and when $|k|$ is reduced to the value $(\lambda/2)$, the asymptotic wave function will cease to have the form (4-113) and at this energy $K_{\beta a}$ will possess a branch point. If we continue below n of the original N open channels, a new matrix of dimension $M = N - n$ may be defined by

equations (4-76). This matrix will be denoted by $\bar{\mathbf{K}}^M$ and called the reduced K-matrix. The original $\mathbf{K}$ matrix, of dimensions $N \times N$, continued into the same region will be denoted by $\mathbf{K}^N$. To relate the two matrices, we partition $\mathbf{K}^N$ by

$$\mathbf{K}^N = \begin{pmatrix} \mathbf{K}^{MM}, & \mathbf{K}^{Mn} \\ \mathbf{K}^{nM}, & \mathbf{K}^{nn} \end{pmatrix}, \qquad (4-114)$$

where K^{RS} denotes a matrix of dimensions $R \times S$. The connection is obtained by observing that the transition matrix for the M open channels must have the same value whether computed from K^N or $\bar{K}^M$. It follows that

$$\bar{\mathbf{K}}^M = \mathbf{K}^{MM} + i\mathbf{K}^{Mn} \frac{1}{1 - i\mathbf{K}^{nn}} \mathbf{K}^{nM}. \qquad (4-115)$$

This relation is obvious for two channels, and a general proof may be given by expanding the transition matrix in powers of $\mathbf{K}$ (Dalitz, 1961).

Poles in the reduced matrix $\bar{\mathbf{K}}^M$ on the real axis give rise to poles in $\mathbf{T}$ which are observed, as we have seen, as resonances in the cross section. A pole in $\bar{\mathbf{K}}^M$ may be due to a pole in the original reaction matrix $\mathbf{K}^N$, in which case each element of $\mathbf{K}^N$ is a rapidly varying function of energy. Alternatively, if the condition

$$\det \left| \mathbf{1} - i\mathbf{K}^{nn} \right| = 0, \qquad (4-116)$$

is satisfied at a particular energy, a pole will appear in $\bar{\mathbf{K}}^M$ without any element of the original matrix $\mathbf{K}^N$ exhibiting a rapid variation with energy. If there were no coupling to other channels, the energies for which (4-116) is satisfied would be the energies of the real bound states of the n closed channel system, since at these energies the exponentially increasing part of the wave function vanishes and the wave function for the n coupled closed channels is normalizable. When the coupling is switched on, the poles in the transition matrix move off the real energy axis and the resonances produced are said to be due to 'virtual bound states'.

It is interesting to examine the analytic structure of the $\mathbf{S}$ matrix as a function of k rather than of E. If there are just

two channels labelled 1 and 2, then

$$k_1^2 = k_2^2 + a \quad (a > 0), \tag{4-117}$$

where a is a constant. Each matrix element of **S** can be considered either as a function of k_1 or of k_2. As a function of k_1, there will be branch points on the real axis at $k_1 = \pm\sqrt{a}$, which may be joined by a branch cut as shown in Fig. 4-2. As
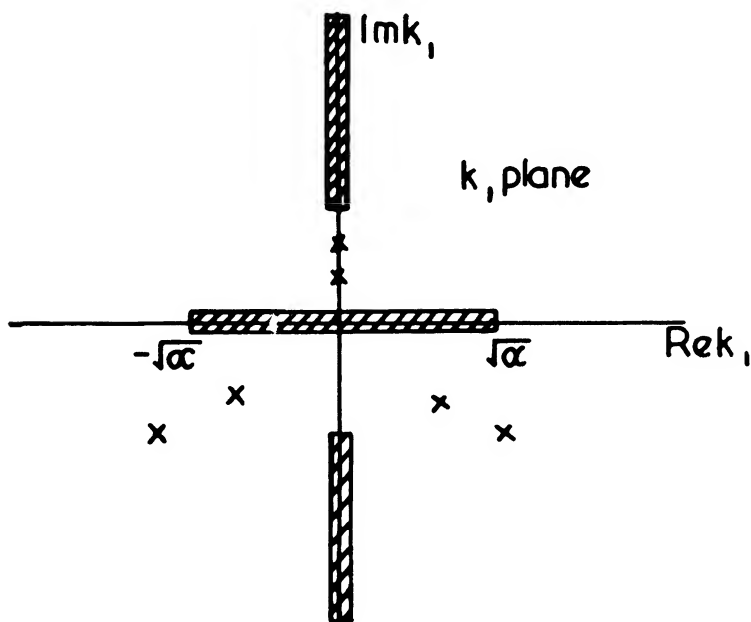
Figure 4-2   The structure of the **S** matrix when there are two open channels.

a function of k_2, the branch points will be on the imaginary axis from $-i\sqrt{a}$ to $+i\sqrt{a}$ If the two channels were decoupled ($S_{12} = S_{21} = 0$), the bound state poles in $S_{22}(k_2)$ would lie on the imaginary k_2 axis (Im$k_2 > 0$), or correspondingly as a function of k_1 on the real k_1 axis between $\pm\sqrt{a}$, on the cut. When the coupling is switched on, these poles will migrate from the real k_1 axis into the lower half k_1 plane, giving rise to resonances. This phenomena is of great importance in the

theory of electron atom collisions and we shall encounter
several examples in the following chapters. Ross and Shaw
(1961) have made an interesting numerical study of the case
of two coupled channels with square well potentials, and they
have shown in detail how the various effects we have discussed
vary with potential range and strength and they have discussed
the limits of usefulness of the effective range expansion of the
M matrix. In particular they have given arguments that sug-
gest that the diagonal elements of **R₀** the effective range
matrix are much more important than the off-diagonal elements,
which may often be neglected.

4-6   THE THREE BODY PROBLEM AND THE FADDEEV EQUA-TIONS

In the following chapters it will be shown that many
practical approximations for treating many-body scattering
problems can be based on the variational method, or on the
truncation of infinite sets of coupled equations, such as equa-
tions (4-75). For many purposes, it would be desirable to
attempt to solve the integral equations for the transition matrix
or for the Green's functions directly, and we saw in Chapters
1 and 2 that this could be done rather easily in the case of
potential scattering, because the equations were of Fredholm
form, which implies, among other things, that numerical solu-
tions can be obtained by approximating the integration by a
sum, and solving the resulting simultaneous linear equations
by matrix inversion. As we shall see, in the many-body case
the situation is not straightforward, because the kernels of the
integral equations are highly singular, and not of Fredholm
form. These difficulties appear first in the three-body system,
which we shall study as the prototype of many-body scattering.
Among the scattering processes that can occur between three
particles are those in which two particles interact together,
while the third particle passes undisturbed. In momentum
space, this physical situation is represented by the
presence of delta functions in the kernel of the equation, show-
ing that the momentum of the unscattered particle is conserved.
These terms are illustrated by Fig. 4-3, which represents a
kernel of the form $\delta(\mathbf{k}_1 - \mathbf{k}_1') K(\mathbf{k}_2, \mathbf{k}_3; \mathbf{k}_2', \mathbf{k}_3')$. In the
diagram the blob represents the interaction between the pair of
particles (2 + 3), while the straight line with no blob
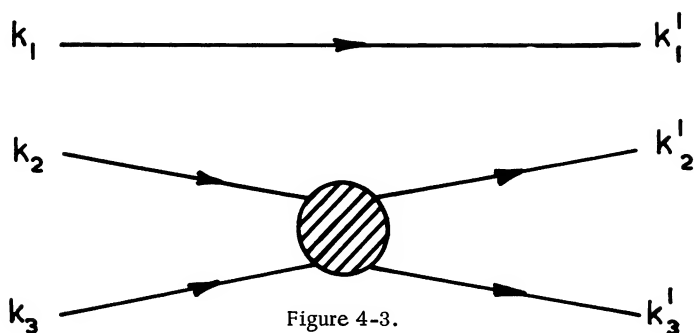
Figure 4-3.

represents the non-interacting particle 1. A kernel, for which the corresponding diagram contains lines that have no blobs representing interactions, is said to be disconnected.

Before we can see how disconnected terms arise and the difficulties associated with them, it is necessary to introduce some notation. We shall consider a system of three spinless particles, 1, 2 and 3, with masses m_1, m_2 and m_3 and position vectors $\mathbf{r}_1$, $\mathbf{r}_2$ and $\mathbf{r}_3$ respectively, and the interaction between particles i and j will be denoted by V_{ij}. The momentum of particle i will be denoted by $\hbar\mathbf{k}_i$, and we shall work in the center of mass system in which

$$\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 = 0. \tag{4-118}$$

As only two of the momenta $\mathbf{k}_1$, $\mathbf{k}_2$ and $\mathbf{k}_3$ are independent, it is more convenient to introduce momentum coordinates ($\mathbf{p}_1$, $\mathbf{q}_1$) defined by

$$\mathbf{p}_1 = \frac{1}{(m_2 + m_3)}(m_3 \mathbf{k}_2 - m_2 \mathbf{k}_3),$$

$$\mathbf{q}_1 = \frac{1}{(m_1 + m_2 + m_3)} \{m_1 (\mathbf{k}_2 + \mathbf{k}_3) - (m_2 + m_3)\mathbf{k}_1\}. \tag{4-119a}$$

The momentum $\mathbf{p}_1$ is the center of mass momentum in the two particle sub-system (2 + 3), while $\mathbf{q}_1$ is the momentum of particle 1 relative to the center of mass of the (2 + 3) sub-system. The momenta $\mathbf{p}_1$ and $\mathbf{q}_1$ are conjugate to the center of mass coordinates $\mathbf{S}_1$ and $\mathbf{R}_1$, where

$$\mathbf{S}_1 = \mathbf{r}_2 - \mathbf{r}_3,$$

$$\mathbf{R}_1 = -\mathbf{r}_1 + \frac{1}{(m_2 + m_3)}(m_2 \mathbf{r}_2 + m_3 \mathbf{r}_3). \tag{4-119b}$$

The vector $\mathbf{S}_1$ is the relative position vector of the particles in the sub-system (2 + 3), while $\mathbf{R}_1$ is the position vector of 1 with respect to the center of mass of (2 + 3).

Plainly, alternative sets of momenta can be introduced, $(\mathbf{p}_2, \mathbf{q}_2)$ or $(\mathbf{p}_3, \mathbf{q}_3)$, in which $\mathbf{p}_2$ is the center of mass momentum in the sub-system $(1 + 3)$, and $\mathbf{q}_2$ is the relative momentum of 2 with respect to the center of mass of $(1 + 3)$, while $\mathbf{p}_3$ is the center of mass momentum in the sub-system $(1 + 2)$ and $\mathbf{q}_3$ is the relative momentum of particle 3 with respect to this subsystem. In the same way, corresponding center of mass coordinates $(\mathbf{S}_2, \mathbf{R}_2)$, $(\mathbf{S}_3, \mathbf{R}_3)$, can be defined. Expressions for $(\mathbf{p}_i, \mathbf{q}_i)$, $(\mathbf{S}_i, \mathbf{R}_i)$ can be obtained from equations (4-119a,b) by cyclic permutation of the suffices 1, 2 and 3.

The three sets of momenta are linearly dependent and we can transform from one set to another using the equations

$$\mathbf{p}_i = \lambda_{ij} \mathbf{p}_j + \eta_{ij} \mathbf{q}_j,$$

$$\mathbf{q}_i = \bar{\lambda}_{ij} \mathbf{p}_j + \bar{\eta}_{ij} \mathbf{q}_j. \qquad (4\text{-}120)$$

We shall not stop to tabulate the coefficients λ_{ij}, $\bar{\lambda}_{ij}$, η_{ij} and $\bar{\eta}_{ij}$ which depend only on the masses m_i and which can be obtained easily by the reader.

In forming integral equations, we shall often require several independent sets of momenta. We shall use the convention that sets of momenta with different numbers of primes attached will be independent of one another. That is to say that the three sets of momenta $(\mathbf{p}_i, \mathbf{q}_i)$, $i = 1, 2, 3$ will be linearly dependent, but will be independent of the three sets $(\mathbf{q}_i', \mathbf{p}_i')$, and so on.

Having disposed of these somewhat lengthy notational problems, we can examine the matrix elements of the kinetic and potential energy operators in the basis of the plane wave states[6] $|\mathbf{p}_i, \mathbf{q}_i\rangle$. The kinetic energy operator $\mathbf{K}$ is diagonal in each of the three sets of momenta and we have

$$\langle \mathbf{p}_i, \mathbf{q}_i | \mathbf{K} | \mathbf{p}_i', \mathbf{q}_i' \rangle = \left(\frac{\hbar^2}{2 M_i} p_i^2 + \frac{\hbar^2}{2 \mu_i} q_i^2 \right) \delta(\mathbf{p}_i - \mathbf{p}_i') \delta(\mathbf{q}_i - \mathbf{q}_i'), \quad (4\text{-}121)$$

where the reduced masses M_i and μ_i are defined by

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[6] In configuration space the state $|\mathbf{p}_i, \mathbf{q}_i\rangle$ is represented by the plane wave function $(2\pi)^{-3} \exp[i(\mathbf{p}_i \cdot \mathbf{S}_i + \mathbf{q}_i \cdot \mathbf{R}_i)]$.

$$M_i = \frac{m_j m_k}{(m_j + m_k)} \, ,$$

$$\mu_i = \frac{m_i(m_j + m_k)}{m_i + m_j + m_k} \, , \qquad i = 1,2,3; \quad i \neq j \neq k. \tag{4-122}$$

The two body potential $V_{ij}(S_k)$, $i \neq j \neq k$, is diagonal in the momentum q_k, and the matrix element of V_{ij} in the basis $|p_k, q_k\rangle$ is given by

$$\langle p_k, q_k | V_{ij} | p'_k, q'_k \rangle = (2\pi)^{-6} \int dR_k \int dS_k \, e^{-i(p_k \cdot S_k + q_k \cdot R_k)}$$

$$V_{ij}(S_k) e^{+i(p'_k \cdot S_k + q'_k \cdot R_k)} \tag{4-123a}$$

$$= \delta(q_k - q'_k) v_{ij}(p'_k - p_k),$$

where v_{ij} is the Fourier transform of the potential

$$v_{ij}(p) = (2\pi)^{-3} \int dx \, V_{ij}(x) \exp(ik \cdot x). \tag{4-123b}$$

The Green's function

The complete Green's function for the system G^+, defined by

$$G^+(E) = (E + i\epsilon - K - V_{12} - V_{23} - V_{31})^{-1}, \tag{4-124}$$

satisfies integral equations of the general form (4-38). In particular, if in (4-38) we set V_γ equal to the complete interaction, and G_γ^+ equal to G_0^+, the free particle Green's function, it is found that G^+ satisfies the equation

$$G^+ = G_0^+ + G_0^+(V_{12} + V_{23} + V_{31})G^+, \tag{4-125}$$

where G_0^+ is, as usual, defined as

$$G_0^+(E) = (E + i\epsilon - K)^{-1}. \tag{4-126}$$

The formal solution of equation (4-125) is

$$G^+(E) = RG_0(E),\qquad\qquad(4\text{-}127)$$

where the resolvent R is the operator

$$R = [1 - G_0^+(V_{12} + V_{23} + V_{31})]^{-1}.\qquad\qquad(4\text{-}128)$$

If we wished to construct R using Fredholm's theory, we would have to consider the determinant

$$D(E) = \det(1 - G_0^+(V_{12} + V_{23} + V_{31})),\qquad\qquad(4\text{-}129)$$

and for this to exist $\mathrm{Tr}\{G_0^+(V_{12} + V_{23} + V_{31})\}$ must be finite. The matrix element of $(G_0^+V_{23})$ is, using (4-121) and (4-123),

$$\langle \mathbf{p}_1,\mathbf{q}_1 | G_0^+V_{23} | \mathbf{p}_1',\mathbf{q}_1' \rangle = \left(E + i\epsilon - \frac{p_1^2}{2M_1} - \frac{q_1^2}{2\mu_1}\right)^{-1} v_{23}(\mathbf{p}_1 - \mathbf{p}_1') \times$$

$$\times\ \delta(\mathbf{q}_1 - \mathbf{q}_1').\qquad\qquad(4\text{-}130)$$

Because of the presence of the delta function $\delta(\mathbf{q}_1 - \mathbf{q}_1')$ the trace of this term does not exist. In the same way the traces of each of the terms $(G_0^+V_{12})$ and $(G_0^+V_{13})$, are also divergent, and it follows that Fredholm's theory cannot be applied to the kernel $\{G_0^+(V_{12} + V_{23} + V_{31})\}$.

The Born series

The presence of disconnected terms in the kernel also causes difficulties in the discussion of the Born series for rearrangement collisions.[7] If we consider a transition between an initial state φ_1 in which free particle 1 moves with respect to a bound state of the sub-system $(2 + 3)$ and a final state φ_3, in which particle 3 moves with respect to a bound state of the sub-system $(1 + 2)$, the transition matrix T_{31} is given, using (4-37), by

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[7] The Born series for rearrangement collisions are discussed in considerable detail by Bransden (1965, 1969).

$$T_{31} = B_{31} + \langle \varphi_3 | (V_{31} + V_{32}) G^+ (V_{12} + V_{13}) | \varphi_1 \rangle, \quad (4-131)$$

where B_{31} is the first Born approximation to the transition matrix

$$B_{31} = \langle \varphi_3 | (V_{31} + V_{32}) | \varphi_1 \rangle. \qquad (4-132)$$

By introducing a complete set of plane wave intermediate states, T_{31} can be written as

$$T_{31} = B_{31} + \int d\mathbf{p}_1 \int d\mathbf{p}_1' \int d\mathbf{q}_1 \int d\mathbf{q}_1' \, \langle \varphi_3 | (V_{31} + V_{32}) | \mathbf{p}_1, \mathbf{q}_1 \rangle \times$$

$$\times \langle \mathbf{p}_1, \mathbf{q}_1 | G^+ | \mathbf{p}_1', \mathbf{q}_1' \rangle \langle \mathbf{p}_1', \mathbf{q}_1' | (V_{12} + V_{13}) | \varphi_1 \rangle. \quad (4-133)$$

Because φ_3 and φ_1 contain bound states of the $(1 + 2)$ and $(2 + 3)$ sub-systems respectively, there is no restriction on the values of the momenta in the intermediate states and the integrations in (4-133) are over all values of $\mathbf{p}_1, \mathbf{p}_1', \mathbf{q}_1$ and $\mathbf{q}_1'$.

Now the Born series for G^+ is obtained by iterating the integral equation (4-125). It is

$$G^+ = G_0^+ + G_0^+ (V_{12} + V_{23} + V_{31}) G_0^+ +$$

$$+ G_0^+ (V_{12} + V_{23} + V_{31}) G_0^+ (V_{12} + V_{23} + V_{31}) G_0^+ + \ldots,$$

$$(4-134)$$

and by inserting this series into (4-131) the Born series for the transition matrix is obtained.

As a consequence of the disconnected nature of the kernel of the integral equation for G^+, among the various sub-series in (4-134) are those that represent successive scattering by one potential only. For example the sub-series containing V_{23} is

$$\{ G_0^+ + G_0^+ V_{23} G_0^+ + G_0^+ V_{23} G_0^+ V_{23} G_0^+ + \ldots \}. \qquad (4-135)$$

This series can be summed formally, and denoting the sum by $G_1^+(E)$, we have

$$G_1^+(E) = (E + i\epsilon - \mathbf{K} - V_{23})^{-1}. \qquad (4-136)$$

This is a three-body Green's operator for a system in which the only potential acting is that between particles $(2 + 3)$.

The matrix element of G_1^+ in the basis $| \mathbf{p}_1, \mathbf{q}_1 \rangle$ is diagonal in $\mathbf{q}_1$ and we can write, using (4-121) and (4-123),

$$\langle \mathbf{p}_1, \mathbf{q}_1 | G_1^+ | \mathbf{p}_1', \mathbf{q}_1' \rangle = \delta(\mathbf{q}_1 - \mathbf{q}_1') \langle \mathbf{p}_1 | g_1^+ \left(E - \frac{q_1'^2}{2\mu_1} \right) | \mathbf{p}_1' \rangle,$$

$$(4-137)$$

where $g_1^+(z)$ is defined as

$$g_1^+(z) = (z + i\epsilon - K_{23} - V_{23})^{-1}, \qquad (4-138)$$

and where K_{23} is the kinetic energy operator associated with the particles 2 and 3 in their center of mass system. The matrix element of K_{23} is

$$\langle \mathbf{p}_1 | K_{23} | \mathbf{p}_1' \rangle = \delta(\mathbf{p}_1 - \mathbf{p}_1') \left(\frac{p_1^2}{2 M_1} \right).$$

The Green's function $g_1^+(z)$ operates in the two particle subspace $(2 + 3)$ only, and is the Green's function appropriate to the scattering of a single particle by the potential V_{23}, which was discussed extensively in Chapter 1. In particular, we know that $g_1^+(z)$ has a pole at $z = E_B$ where E_B is the binding energy of the bound system $(2 + 3)$.   Because of this pole   the Born expansion of $g_1^+(z)$ certainly diverges for z in the range $|z| < |E_B|$. As the $|\mathbf{q}'|$ integration in (4-133) is over the range $0 \leq |\mathbf{q}_1'| \leq \infty$, for each energy E there will be a range of $|\mathbf{q}_1'|$ for which $0 \leq |E - (q_1'^2/2\mu_1| < |E_B|$ and it follows that in this interval the expansion of $g^+(z)$ diverges and that the sub-series (4-135) in G^+ also diverges.

 As all the remaining terms in the expansion of G^+ involve V_{12} or V_{31} these terms cannot compensate, in general, for the divergence in the sub-series in V_{23}. It follows that the expansion of G^+ necessarily diverges at all energies E, for some ranges of the variables $\mathbf{p}_1$, $\mathbf{q}_1$, $\mathbf{p}_1'$, $\mathbf{q}_1'$. The divergence of the expansion of G^+ makes the convergence of the series for the transition matrix doubtful. Little is known about the convergence of the Born series for the transition matrix, but recently Dettmann and Leibfried (1969), in an important paper, have been able to demonstrate in the case of a wide class of potentials that the energy variation of T_{31} is given correctly at sufficiently large energies, by the first two terms of the Born series. It is not clear whether the series itself converges at high energies, or whether it is an asymptotic (semi-convergent) series, but it is clear that except for special

values of the masses the use of the first Born approximation is unjustified in the case of rearrangement collision at any energy.

Removal of disconnected terms

The poor properties of the integral equation (4-125) for G^+ arise from terms in an expansion, such as (4-134) in which only one potential operates. These sub-series can be formally summed as in the expression for G_1^+ (4-135). The Green's function G_1^+ and the corresponding operators G_2^+ and G_3^+ can be defined as

$$G_i^+(E) = (E + i\epsilon - \mathbf{K} - V_{jk})^{-1}, \quad i \neq j \neq k. \tag{4-139a}$$

In the three-body system, these operators are identical with those introduced earlier in this chapter, by equation (4-12). It is straightforward to verify that G_i^+ satisfies integral equations of the standard type:—

$$G_i^+ = G_0^+(1 + V_{jk}G_i^+) = (1 + G_i^+V_{jk})G_0^+, \quad i \neq j \neq k. \tag{4-139b}$$

The general method for finding an integral equation for the three-body problem that has a connected kernel, is to make use of the fact that the operators G_i^+ can be constructed exactly, by the methods developed for potential scattering and described in Chapters 1 and 2, to eliminate all the divergent sub-series in expansions like (4-134).

Let us first examine in more detail the problem of scattering in which a potential acts between one pair of particles only. The Green's function $g_1^+(z)$, for potential scattering between particles 2 and 3 in their center of mass system, has been introduced in (4-138). In the same way, $g_2^+(z)$ and $g_3^+(z)$ describing the interaction of particles $(1 + 3)$ and $(1 + 2)$ can be defined, by

$$g_i^+(z) = (z + i\epsilon - \mathbf{K}_{jk} - V_{jk})^{-1}, \quad i \neq j \neq k. \tag{4-140}$$

The corresponding two-body transition operators $t_i(z)$ can be introduced as

$$t_i(z) = V_{jk} + V_{jk}g_i^+(z)V_{jk}, \quad i \neq j \neq k. \tag{4-141}$$

We shall suppose the three two-body problems have been

solved and that the $t_i(z)$ and their matrix elements $\langle \mathbf{p}_i | t_i(z) | \mathbf{p}_i' \rangle$ are known exactly.

To calculate the scattering amplitude for potential scattering, we must satisfy the conservation of energy condition

$$z = \frac{p_i^2}{2M_i} = \frac{p_i'^2}{2M_i}.$$

When this condition is satisfied $\langle \mathbf{p}_i | t_i(z) | \mathbf{p}_i' \rangle$ is said to be 'on the energy shell'. In the applications that follow, we require this matrix element for independent values $\mathbf{p}_i$, $\mathbf{p}_i'$ and z not constrained by the conservation of energy condition, and in this case $\langle \mathbf{p}_i | t_i(z) | \mathbf{p}_i' \rangle$ is said to be 'off the energy shell'.

The Green's functions G_i^+, which relate to a three-body system in which only one potential is acting, are now determined by equations typified by (4-137). In general we have

$$\langle \mathbf{p}_i, \mathbf{q}_i | G_i^+(E) | \mathbf{p}_i', \mathbf{q}_i' \rangle = \delta(\mathbf{q}_i - \mathbf{q}_i') \langle \mathbf{p}_i | g_i^+(E - q_i^2/2\mu_i) | \mathbf{p}_i' \rangle.$$

$$(4\text{-}142)$$

It is important to notice that the analytic structure of G_i^+ is different from that of g_i^+. At a bound state of the two particle system $g_i^+(z)$ must have a pole, at $z = E_B$, say, but G_i^+ will possess a line of singularities (a branch cut) because the argument of g_i^+ in (4-140) depends on $(E - q_i^2/2\mu_i)$, which is a function of q_i^2. This cut runs over the real energy axis in the interval $E_B \le E < \infty$, and represents the physical cut associated with the scattering of the third particle by the two-body bound sub-system.

Three transition operators T_i can be associated with the Green's functions G_i by the definitions

$$T_i = V_{jk} + V_{jk} G_i^+(E) V_{jk}, \quad i \neq j = k. \qquad (4\text{-}143a)$$

For future reference we note that a slight manipulation of this equation leads to the results

$$G_0^+T_i = G_i^+V_{jk},$$
$$\qquad\qquad i \neq j \neq k, \qquad\qquad (4\text{-}143\text{b})$$
$$T_iG_0^+ = V_{jk}G_i^+,$$

where we have made use of the integral equations (4-139b).

The matrix elements of the T_i can be expressed in terms of the two-body transition operators t_i, since

$$\langle \mathbf{p}_i, \mathbf{q}_i | T_i(E) | \mathbf{p}_i', \mathbf{q}_i' \rangle = \delta(\mathbf{q}_i - \mathbf{q}_i') \langle \mathbf{p}_i | t_i(E - q_i^2/2\mu_i) | \mathbf{p}_i' \rangle.$$

$$(4\text{-}144)$$

The resolvents R_i of the integral equations satisfied by G_i^+ and T_i^+ are defined as

$$R_i(E) = (1 - G_0^+(E)V_{jk})^{-1}, \quad i \neq j \neq k, \qquad (4\text{-}145)$$

and we have that

$$G_i^+ = G_0^+(1 + V_{jk}G_i^+) = R_iG_0^+,$$
$$\qquad\qquad i \neq j \neq k \qquad (4\text{-}146)$$
$$T_i = V_{jk} + V_{jk}G_i^+V_{jk} = V_{jk}R_i.$$

These resolvents clearly exist and can be constructed in principle. The Fredholm determinants of the resolvents are non-singular in the two particle sub-spaces in which the potentials V_{jk} act. It should be noted that because the resolvents contain delta functions in $\mathbf{q}_i$ the Fredholm determinants are not defined in the complete space of the three particles.

The determinantal method

The first method[8] to be discussed is the extension of the determinantal method discussed in Chapter 2. The idea is to introduce two arbitrary operators L and M and to write the resolvent of the three-body system (4-128) as

$$R = L[M\{1 - G_0^+(V_{12} + V_{23} + V_{31})\}L]^{-1}M. \qquad (4\text{-}147)$$

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[8] This section is based on the work of Sugar and Blankenbecler (1963).

We can then try to choose L and M so that M^{-1} and the determinant $D(E)$ exist, where

$$D(E) \equiv \det(M\{1 - G_0^+(V_{12} + V_{23} + V_{31})\}L). \qquad (4\text{-}148)$$

These conditions ensure that the inverse of the operator $(M\{1 - G_0^+(V_{12} + V_{23} + V_{31}\}L)$ can be constructed, which in turn allows us to construct R through equations (4-147). There are many possible ways in which M and L can be chosen. One possibility is to set

$$L = 1, \quad M = (1 + C)(R_1 + R_2 + R_3 - 2), \qquad (4\text{-}149)$$

where C will be chosen in a moment, and the R_i are the resolvents defined by (4-145), which can be calculated in terms of two-body scattering. We then find after a little algebra that

$$M\{1 - G_0^+(V_{12} + V_{23} + V_{31})\}L = (1 + C)(1 - C_0), \qquad (4\text{-}150)$$

where

$$\begin{aligned}
C_0 = G_0^+ \{ & V_{23}R_1 G_0^+(V_{12} + V_{31}) \\
& + V_{31}R_2 G_0^+(V_{32} + V_{21}) \\
& + V_{12}R_3 G_0^+(V_{23} + V_{31}) \}.
\end{aligned} \qquad (4\text{-}151)$$

This operator contains no disconnected parts, since different potentials occupy adjacent positions in the kernel, and in a series expansion of C_0 we find no sub-series in which one potential acts alone. These sub-series have in fact already been summed and are represented in the known resolvents R_i. The operator C can now be chosen so that the trace of $(1 + C)(1 - C_0)$ exists. A possible choice is $C = C_0$, and the leading term in the trace is then $\mathrm{Tr}(C_0^2)$. As this contains the product of four potentials, it will exist given reasonable behaviour at the origin and at infinity.

An application of this method has been made to electron hydrogen atom scattering (Nutt, 1964), and for practical details reference may be made to the original paper.

The Faddeev equations

We shall discuss the approach of Faddeev (1958, 1963), in the form developed by Lovelace (1964). To start we must define transition operators for all the possible reactions that can occur between three particles. The transition operators will be written as $U_{\beta\alpha}(E)$, where the suffix α is 1, when the initial state is in the arrangement in which particle 1 moves with respect to a bound state of sub-system $(2 + 3)$, 2 when particle 2 moves with respect to a bound state of $(3 + 1)$, and 3 when particle 3 moves with respect to a bound state $(2 + 1)$. The suffix β can also take the values 1, 2 or 3 and describes the possible final states in which particles 1, 2 or 3 are free. Reactions can also occur in which all three particles are unbound in either the initial or final state, or both, and these channels will be denoted by setting α or β equal to 0.

The interaction potential in channel γ (cf. 4-4, 4-5) is denoted by $V\gamma$ and is equal to the difference of the complete interaction, $(V_{12} + V_{13} + V_{23})$, and the potential between the pair of bound particles. In channel 0 where no particles are bound the interaction V_0 is equal to the complete interaction.

$$V_0 = V_{12} + V_{23} + V_{31}$$
$$V_1 = V_{12} + V_{13}$$
$$V_2 = V_{23} + V_{21}$$
$$V_3 = V_{31} + V_{32}.$$

$$(4-152)$$

The transition operators then satisfy the equations[9] (see 4-37)

$$U_{\beta\alpha}(E) = V_\alpha + V_\beta G^+(E)V_\alpha, \quad \alpha, \beta = 0, 1, 2, 3 \qquad (4-153)$$

where $G^+(E)$ can be determined by the integral equations (4-38)

$$G^+ = G_\gamma^+(1 + V_\gamma G^+) \qquad (4-154)$$

and the G_γ^+ are defined by (4-139a,b) (see also 4-12). The

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[9] We have arbitrarily chosen to work with the operators $U_{\beta\alpha}$ rather than $\bar{U}_{\beta\alpha}$, where $\bar{U}_{\beta\alpha} = V_\beta + V_\beta G^+(E)V_\alpha$. The matrix elements of these operators are not the same off the energy shell, but the same physical on shell scattering amplitude is derived from either operator.

matrix elements of all these operators are to be taken with
respect to sets of plane wave states $|\mathbf{p}_i, \mathbf{q}_i\rangle$ as before. To
compute the physical transition matrix T_{12} (E) for a reaction in
which the initial state is in channel 2 and the final state in
channel 1, we need the momentum space wave functions φ_{13}
and φ_{23} of the initial and final bound states of the (2 + 3) and
(1 + 3) sub-systems. We then have

$$T_{12}(\mathbf{q}_1, \mathbf{q}_2') = \int d\mathbf{p}_1 \int d\mathbf{p}_2' \, \varphi_{23}(\mathbf{p}_1) \langle \mathbf{p}_1, \mathbf{q}_1 | U_{12}(E) | \mathbf{p}_2', \mathbf{q}_2' \rangle \varphi_{13}(\mathbf{p}_2').$$

$$(4\text{-}155)$$

The primed and unprimed momenta are independent, but for
physical scattering the conservation of energy relation must be
satisfied,

$$\epsilon_{23} + \frac{\hbar^2}{2\mu_1} q_1^2 = \epsilon_{13} + \frac{\hbar^2}{2\mu_2} q_2'^2 \,,$$

where ϵ_{23} and ϵ_{13} are the binding energies in the (2 + 3) and
(3 + 1) sub-systems. The scattering amplitude for any other
reaction can be written down in a similar way.

The important step in the Faddeev method is the elimi-
nation of the potentials in the kernel of equation (4-153).
Taking the equation for $U_{12}(E)$ and writing it in full, we have

$$U_{12} = (V_{23} + V_{21}) + (V_{12} + V_{13})G^+(V_{23} + V_{21}). \quad (4\text{-}156)$$

In the term containing $V_{12}G^+$, we use the integral equation
(4-154) for G^+ with γ set equal to 3 and in the term containing
$V_{13}G^+$ we use the same equation, but with γ set equal to 2.
We then obtain

$$U_{12} = (V_{23} + V_{21}) + [V_{12}G_3^+ + V_{12}G_3^+(V_{31} + V_{32})G^+ +$$

$$+ V_{13}G_2^+ + V_{13}G_2^+(V_{23} + V_{21})G^+](V_{23} + V_{21}).$$

$$(4\text{-}157)$$

On using equations (4-153) we then find that

$$U_{12} = (V_{23} + V_{21}) + V_{12}G_3^+U_{32} + V_{13}G_2^+U_{22}.$$

Looking back at equation (4-143b), it is seen that the operators
$V_{12}G_3^+$ and $V_{13}G_2^+$ are equal to $T_3G_0^+$ and $T_2G_0^+$ respectively,
so we may write finally

$$U_{12} = (V_{23} + V_{21}) + T_3 G_0^+ U_{32} + T_2 G_0^+ U_{22}$$

$$= V_2 + \sum_{\gamma=1}^{3} \left(1 - \delta_{1\gamma}\right) T_\gamma G_0^+ U_{\gamma 2}. \tag{4-158}$$

Proceeding in the same way, we find generally,

$$U_{\beta\alpha} = V_\alpha + \sum_{\gamma=1}^{3} \left(1 - \delta_{\beta\gamma}\right) T_\gamma G_0^+ U_{\gamma\alpha}. \tag{4-159}$$

To include the channels in which all three particles are unbound we write

$$T_0 = 0, \tag{4-160}$$

and then the suffices α, β and γ can be allowed to take values from 0 to 3, rather than from 1 to 3.

The equations (4-159) are in a form due to Lovelace (1964) and are equivalent to the original equations of Faddeev. It is immediately evident that the kernel of the equations is connected, because on iterating the equation we always obtain terms such as

$$\dots T_\alpha G_0^+ T_\delta G_0^+ \dots , \tag{4-161}$$

where $\alpha \neq \delta$ always, and no sub-series exist in which each term contains a momentum conserving delta function. This is because we have solved all the individual two-body scattering problems first, and we do not attempt to expand the operators T_γ, which would reintroduce the disconnected terms.

It is possible to write equations in which the inhomogeneous terms contain the two-body transition operators T_γ rather than the potentials V_γ. To see how this is done, let us concentrate on the three transition matrices $U_{\alpha 2}$ that describe processes in which the initial state is in channel 2, which is the arrangement in which particle 2 moves with respect to a bound state of $(1 + 3)$. Three auxiliary operators $W_{\alpha 2}(E)$ are introduced through the definitions

$$W_{12}(E) = V_{32} + V_{32} G^+(E)(V_{23} + V_{21})$$

$$W_{22}(E) = V_{13} G^+(E)(V_{23} + V_{21}) \tag{4-162}$$

$$W_{32}(E) = V_{12} + V_{12} G^+(E)(V_{23} + V_{21}).$$

From equation (4-156) it is seen that U_{12} (E) can be expressed in terms of the $W_{\beta 2}$ by

$$U_{12}(E) = (V_{23} + V_{12}) + (W_{22} + W_{32} - V_{12}) = V_{23} + W_{22} + W_{32}$$

Similarly U_{22}, U_{32} and U_{02} are expressed as

$$U_{22} = W_{12} + W_{32},$$

$$U_{32} = V_{12} + W_{12} + W_{22}, \qquad\qquad (4-163)$$

$$U_{02} = W_{12} + W_{22} + W_{32}.$$

To obtain integral equations for the new quantities $W_{\beta\alpha}$, we again use the integral equation (4-154) for G^+, with V_γ defined by (4-152). We have that

$$W_{12} = V_{23} + V_{23} G^+ (V_{23} + V_{21})$$

$$= V_{23} + V_{23} \{ G_1^+ + G_1^+ (V_{12} + V_{13}) G^+ \} (V_{23} + V_{21})$$

$$= V_{23} + V_{23} G_1^+ V_{23} + V_{23} G_1^+ (W_{32} + W_{22}). \qquad (4-164)$$

Since, (4-143a,b),

$$V_{23} + V_{23} G_1^+ V_{23} = T_1, \qquad\qquad (4-165)$$

and

$$V_{23} G_1^+ = T_1 G_0,$$

we find that

$$W_{12} = T_1 + T_1 G_0^+ (W_{32} + W_{22}). \qquad\qquad (4-166a)$$

In an exactly similar manner, we find

$$W_{22} = T_2 G_0^+ (W_{12} + W_{32}), \qquad\qquad (4-166b)$$

$$W_{32} = T_3 + T_3 G_0^+ (W_{22} + W_{12}). \qquad\qquad (4-166c)$$

In general, if the incident channel is channel β, we find

$$W_{\alpha\beta} = T_\alpha \left(1 - \delta_{\alpha\beta} \right) + T_\alpha G_0^+ \sum_{\gamma=1}^{3} \left(1 - \delta_{\alpha\gamma} \right) W_{\gamma\beta}, \qquad (4-167)$$

$$\alpha, \beta = 1, 2, 3.$$

The kernel of these equations is similar to that of equations (4-159) and the iterative solution contains no successive scatterings by the same two-body potential. In principle, the solution of these equations enables us to calculate the transition matrix

for all excitation, rearrangement or break-up processes, however the equations are of considerable complexity and in practice some simplifications must be made.

Practical calculations

Let us study the particular case where, in the initial configuration, particle 2 moves with respect to a bound state of $(1 + 3)$. Taking matrix elements the Lovelace-Faddeev equations (4-167) become[10]

$$\langle \mathbf{p}_\beta, \mathbf{q}_\beta | W_{\beta 2} | \mathbf{p}_2', \mathbf{q}_2' \rangle = \langle \mathbf{p}_\beta, \mathbf{q}_\beta | T_\beta | \mathbf{p}_2', \mathbf{q}_2' \rangle (1 - \delta_{\beta 2}) +$$

$$+ \sum_{\gamma=1}^{3} \int d\mathbf{p}_\gamma'' \int d\mathbf{q}_\gamma'' \left(1 - \delta_{\beta\gamma}\right) \langle \mathbf{p}_\beta, \mathbf{q}_\beta | T_\beta G_0^+ | \mathbf{p}_\gamma'', \mathbf{q}_\gamma'' \rangle \times \qquad (4\text{-}168)$$

$$\times \langle \mathbf{p}_\gamma'', \mathbf{q}_\gamma'' | W_{\gamma 2} | \mathbf{p}_2', \mathbf{q}_2' \rangle, \qquad \beta = 1, 2, 3$$

where a complete set of states $|\mathbf{p}_\gamma'', \mathbf{q}_\gamma''\rangle$ has been inserted. The momenta $(\mathbf{p}_2', \mathbf{q}_2')$ do not enter the kernels $\langle \mathbf{p}_\beta, \mathbf{q}_\beta | T_\beta G_0^+ | \mathbf{p}_\gamma'', \mathbf{q}_\gamma'' \rangle$, but only enter the inhomogeneous term as parameters. The equations are therefore six dimensional coupled integral equations for the quantities $f_\gamma(\mathbf{p}_\gamma, \mathbf{q}_\gamma)$, where

$$f_\gamma(\mathbf{p}_\gamma, \mathbf{q}_\gamma) \equiv \langle \mathbf{p}_\gamma, \mathbf{q}_\gamma | W_{\gamma 2} | \mathbf{p}_2', \mathbf{q}_2' \rangle. \qquad (4\text{-}169)$$

If we write the inhomogeneous term in the integral equations as $\Phi_\beta(\mathbf{p}_\beta, \mathbf{q}_\beta)$, where

$$\Phi_\beta(\mathbf{p}_\beta, \mathbf{q}_\beta) \equiv \langle \mathbf{p}_\beta, \mathbf{q}_\beta | T_\beta | \mathbf{p}_2', \mathbf{q}_2' \rangle (1 - \delta_{\beta 2}), \qquad (4\text{-}170)$$

the equations become

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[10] In what follows, it is important to observe the convention that sets of momenta bearing the same number of primes are linearly dependent while those with different numbers of primes are independent of each other.

$$f_\beta(\mathbf{p}_\beta, \mathbf{q}_\beta) = \Phi_\beta(\mathbf{p}_\beta, \mathbf{q}_\beta) +$$

$$+ \sum_{\gamma=1}^{3} \int d\,\mathbf{p}_\gamma'' \int d\,\mathbf{q}_\gamma'' \left(1 - \delta_{\beta\gamma}\right) \langle \mathbf{p}_\beta, \mathbf{q}_\beta | T_\beta G_0^+ | \mathbf{p}_\gamma'', \mathbf{q}_\gamma'' \rangle f_\gamma(\mathbf{p}_\gamma'', \mathbf{q}_\gamma'').$$

$$(4-171)$$

A partial wave decomposition of equation (4-171) can be effected,[11] from which coupled integral equations in two scalar variables are found. These equations are still too formidable for the direct application of numerical methods, and in most applications the two-body potentials have been taken to be a sum of separable terms. In this case, the dependence of $f_\gamma(\mathbf{p}_\gamma, \mathbf{q}_\gamma)$ on $\mathbf{p}_\gamma$ is given immediately, and the equations reduce, after an angular momentum decomposition, to coupled equations in a single momentum variable. The use of separable potentials is not such a severe limitation as it first appears, because many local potential $V_{ij}(\mathbf{x})$ can be represented to sufficient accuracy as sum of separable terms. The simplifications that occur will now be illustrated by taking the simple case in which each two-body potential consists of a single separable term,

$$V_{ij} = -u_k(\mathbf{r})u_k(\mathbf{r}'), \qquad i \neq j \neq k. \qquad (4-172)$$

The sign is chosen to that the potential is attractive, and we shall only consider potentials in which $u_k(\mathbf{r})$ is spherically symmetrical.

Separable potentials

In Chapter 2, the scattering of a beam of particles from a separable potential was discussed in a configuration space treatment, but for the present purpose, it is convenient to repeat some of the arguments using a momentum space representation. The Schrödinger equation for a two-body system (labelled by the subscript k) is

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[11] Ahmadzaheh and Tjon (1965).

$$\left(\frac{p_k^2}{2M_k} - E\right)\varphi(\mathbf{p}) = v_k(\mathbf{p})\int d\mathbf{p}'\left\{v_k(\mathbf{p}')\varphi(\mathbf{p}')\right\}, \qquad (4\text{-}173)$$

where $\varphi(\mathbf{p})$ is the momentum space wave function and $v_k(\mathbf{p})$ is the Fourier transform of $u_k(\mathbf{r})$,

$$v_k(\mathbf{p}) = (2\pi)^{-3/2}\int d\mathbf{r}\, u_k(\mathbf{r})\exp(-i\mathbf{p}\cdot\mathbf{r}). \qquad (4\text{-}174)$$

If there is a bound state in the two-body system at energy E_B then, from (4-173), we see at once that the wave function must be

$$\varphi_B(\mathbf{p}) = N\left\{\frac{2M_k v_k(\mathbf{p})}{p^2 - 2M_k E_B}\right\}, \qquad (4\text{-}175)$$

where N is a normalization factor. If φ_B is normalized to unity, then

$$N^{-2} = 4M_k^2\int d\mathbf{p}\left\{\frac{v_k(\mathbf{p})}{p^2 - 2M_k E_B}\right\}^2. \qquad (4\text{-}176)$$

If the solution (4-175) is inserted into the Schrödinger equation, we find an eigenvalue equation for E_B, it is

$$2M_k\int d\mathbf{p}\left\{\frac{[v_k(\mathbf{p})]^2}{p^2 - 2M_k E_B}\right\} = 1. \qquad (4\text{-}177)$$

From the form of the integrand, it is clear that this equation can be satisfied by at most one value of E_B, so that a separable potential of this kind can support only one bound state.

The two-body transition operator t_k satisfies the integral equation

$$t_k = V_{ij} + V_{ij}g_0^+ t_k, \qquad i \neq j \neq k, \qquad (4\text{-}178)$$

where $g_0^+(E)$ is the free particle Green's function for the two-particle system.

It is easily seen that the matrix elements of t_k must

be of the form[12]

$$\langle \mathbf{p} | t_k(E) | \mathbf{p}' \rangle = -J_k(E) v_k(p) v_k(p'). \qquad (4\text{-}179)$$

By substituting into the integral equation (4-178), we have

$$J_k(E) v_k(p) v_k(p') = v_k(p) v_k(p') +$$

$$+ J_k(E) 2M_k v_k(p) \left[\int d\mathbf{p}'' \left\{ \frac{[v_k(p'')]^2}{p^2 - 2M_k E - i\epsilon} \right\} \right] v_k(p'), \qquad (4\text{-}180)$$

which determines $J_k(E)$. It is given by

$$J_k^{-1}(E) = 1 - 2M_k \int d\mathbf{p}'' \left\{ \frac{[v_k(p'')]^2}{p^2 - 2M_k E - i\epsilon} \right\}.$$

Comparing with equation (4-177), it is seen that $J_k^{-1}(E)$ possess a zero when $E = E_B$, which gives rise to a pole in $\langle \mathbf{p} | t_k(E) | \mathbf{p}' \rangle$ at the bound state energy, as expected. The expression (4-179) shows the structure of $\langle \mathbf{p} | t_k | \mathbf{p}' \rangle$ for all $\mathbf{p}, \mathbf{p}'$ and E, not necessarily on the energy shell, and is therefore in just the correct form for use in the Faddeev equations.

The operators T and the three-body kernel

The three-body operators T_γ depend on the two-body scattering operators in each sub-system. In the sub-system k, labelled in the usual way so that $\gamma = 1$ corresponds to particles $(2 + 3)$ and so on, the matrix elements of T_γ are from (4-144, 4-179),

$$\langle \mathbf{p}_\gamma, \mathbf{q}_\gamma | T_\gamma | \mathbf{p}_\gamma', \mathbf{q}_\gamma' \rangle = \delta(\mathbf{q}_\gamma - \mathbf{q}_\gamma') v_\gamma(p_\gamma) v_\gamma(p_\gamma') J_\gamma(E - q_\gamma^2/2\mu_\gamma).$$

$$(4\text{-}181)$$

---

[12] When the potential v_k is spherically symmetrical the matrix element $\langle \mathbf{p} | t_k | \mathbf{p}' \rangle$ does not depend on the scattering angle, or in other words, scattering only takes place in the $\ell = 0$ partial wave.

The kernels of the equations (4-171) now become

$$\langle \mathbf{p}_\beta, \mathbf{q}_\beta | T_\beta G_0^+ | \mathbf{p}_\gamma'', \mathbf{q}_\gamma'' \rangle = \delta(\mathbf{q}_\beta - \mathbf{q}_\beta'') v_\beta(p_\beta) v_\beta(p_\beta'') \times$$

$$\times \frac{J_\beta(E - q_\beta^2/2\mu_\beta)}{E + i\epsilon - p_\gamma''^2/2M_\gamma - q_\gamma''^2/2\mu_\gamma} . \qquad (4\text{-}182)$$

The dependence of the kernel on $\mathbf{p}_\beta$ is given entirely by the multiplicative factor $v_\beta(p_\beta)$. The same is true for the inhomogeneous term Φ_β, since

$$\Phi(\mathbf{p}_\beta, \mathbf{q}_\beta) = \delta(\mathbf{q}_\beta - \mathbf{q}_\beta') v_\beta(p_\beta) v_\beta(p_\beta') J_\beta(E - q_\beta^2/2\mu_\beta)(1 - \delta_{\beta 2}).$$
$$(4\text{-}183)$$

In (4-182), $(\mathbf{p}_\beta'', \mathbf{q}_\beta'')$ are to be expressed in terms of $(\mathbf{p}_\gamma'', \mathbf{q}_\gamma'')$, and in (4-183) $(\mathbf{p}_\beta', \mathbf{q}_\beta')$ are to be expressed in terms of $(\mathbf{p}_2', \mathbf{q}_2')$, using equations (4-120). Comparing the expression for the kernel with the coupled equations (4-171), it is seen that the functions $f_\beta(\mathbf{p}_\beta, \mathbf{q}_\beta)$ can be expressed as

$$f_\beta(\mathbf{p}_\beta, \mathbf{q}_\beta) = F_\beta(\mathbf{q}_\beta) v_\beta(p_\beta) J_\beta(E - q_\beta^2/2\mu_\beta) + \Phi_\beta(\mathbf{p}_\beta, \mathbf{q}_\beta).$$
$$(4\text{-}184)$$

The new functions $F_\beta(\mathbf{q}_\beta)$ are to be determined by substituting this expression in the integral equations (4-171), which leads to the coupled equations,

$$F_\beta(\mathbf{q}_\beta) = \eta_\beta(\mathbf{q}_\beta) + \sum_{\gamma=1}^{3} (1 - \delta_{\beta\gamma}) \int d\mathbf{q}_\gamma'' H_{\beta\gamma}(\mathbf{q}_\beta, \mathbf{q}_\gamma'') F_\gamma(\mathbf{q}_\gamma''),$$

$$\beta = 1, 2, 3. \qquad (4\text{-}185)$$

The kernel of the equation is

$$H_{\beta\gamma}(\mathbf{q}_\beta, \mathbf{q}_\gamma'') = \int d\mathbf{p}_\gamma'' \, \delta(\mathbf{q}_\beta - \mathbf{q}_\beta'') \left\{ \frac{v_\beta(p_\beta'') v_\gamma(p_\gamma'') J_\gamma(E - q_\gamma''^2/2\mu_\gamma)}{E + i\epsilon - p_\gamma''^2/2M_\gamma - q_\gamma''^2/2\mu_\gamma} \right\}.$$
$$(4\text{-}186)$$

The integral can be performed with the help of the delta function $\delta(\mathbf{q}_\beta - \mathbf{q}_\beta'')$, and using the relations (4-120):—

$$H_{\beta\gamma}(\mathbf{q}_\beta, \mathbf{q}_\gamma'') = \left(\frac{1}{\lambda_{\beta\gamma}}\right)^3 \left\{ \frac{v_\beta(p_\beta'')v_\gamma(p_\gamma'')J_\gamma(E - q_\gamma''^2/2\mu_\gamma)}{E + i\epsilon - p_\gamma''^2/2M_\gamma - q_\gamma''^2/2\mu_\gamma} \right\},$$

$$(4\text{-}187a)$$

where everything is expressed in terms of $\mathbf{q}_\beta$ and $\mathbf{q}_\gamma''$, using equations (4-120) and equating $\mathbf{q}_\beta''$ with $\mathbf{q}_\beta$.

The inhomogeneous term is defined by the equation

$$\eta_\beta(\mathbf{q}_\beta) = \sum_{\gamma=1}^{3} \int d\mathbf{p}_\gamma'' \int d\mathbf{q}_\gamma'' \, \delta(\mathbf{q}_\beta - \mathbf{q}_\beta'')(1 - \delta_{\gamma 2})(1 - \delta_{\beta\gamma}) \times$$

$$\times \left\{ \frac{v_\beta(p_\beta'')\bar{\Phi}_\gamma(\mathbf{p}_\gamma'', \mathbf{q}_\gamma'')}{E + i\epsilon - p_\gamma''^2/2M_\gamma - q_\gamma''/2\mu_\gamma} \right\}. \qquad (4\text{-}187b)$$

The integration over both $\mathbf{p}_\gamma''$ and $\mathbf{q}_\gamma''$ can be performed using the delta function $\delta(\mathbf{q}_\beta - \mathbf{q}_\beta'')$ and the delta function $\delta(\mathbf{q}_\gamma'' - \mathbf{q}_\gamma')$, which occurs in $\bar{\Phi}_\gamma$, (see 4-170 and 4-181). The final expression for $\eta_\beta(\mathbf{q}_\beta)$ is:—

$$\eta_\beta(\mathbf{q}_\beta) = \sum_{\gamma=1}^{3}(1 - \delta_{\gamma 2})(1 - \delta_{\beta\gamma})\left(\frac{1}{\lambda_{\beta\gamma}}\right)^3 \left\{ \frac{v_\beta(p_\beta'')v_\gamma(p_\gamma'')J_\gamma(E - q_\gamma''^2/2\mu_\gamma)}{E + i\epsilon - p_\gamma''^2/2M_\gamma - q_\gamma''^2/2\mu_\gamma} \right\}$$

$$(4\text{-}188)$$

In equation (4-188) the set of momenta $(\mathbf{p}_\gamma', \mathbf{q}_\gamma')$ are to be expressed in terms of $(\mathbf{p}_2', \mathbf{q}_2')$, by

$$\mathbf{p}_\gamma' = \lambda_{\gamma 2}\mathbf{p}_2' + \eta_{\gamma 2}\mathbf{q}_2',$$

$$\mathbf{q}_\gamma' = \bar{\lambda}_{\gamma 2}\mathbf{p}_2' + \bar{\eta}_{\gamma 2}\mathbf{q}_2', \qquad (4\text{-}189)$$

while $\mathbf{p}_\beta''$ and $\mathbf{p}_\gamma''$ are functions of $(\mathbf{p}_2', \mathbf{q}_2'$ and $\mathbf{q}_\beta)$ since (using the delta functions)

$$\mathbf{q}_\gamma'' = \mathbf{q}_\gamma'$$

$$\mathbf{p}_\gamma'' = \frac{1}{\bar{\lambda}_{\beta\gamma}}(\mathbf{q}_\beta - \bar{\eta}_{\beta\gamma}\mathbf{q}_\beta'). \qquad (4\text{-}190)$$

The integral equations (4-185) are similar in form to the equations that describe a number of coupled two-body channels. After making an angular momentum decomposition, coupled radial equations are found which can be solved numerically[13]. The whole procedure can be generalized to cover the case in which the potential is a sum of separable terms.

In atomic problems the basic two-body interaction is the Coulomb potential. In order to apply the Faddeev equations, it is necessary as we have seen, to approximate this potential or the two-body transition matrix by a sum or separable terms. This has been discussed by Chen and Ishihara (1968) and we refer the interested reader to the original paper for details.

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[13] The details may be consulted in a paper by Ball, Chen and Wong (1968), where an application to the low energy elastic scattering of electrons by hydrogen atoms is described.

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Chapter 5

SCATTERING OF ELECTRONS
BY ATOMS AT LOW ENERGIES

5-1 THE ELASTIC SCATTERING OF ELECTRONS BY HYDRO-GEN ATOMS

In this chapter, the scattering of electrons which are of energy such that the target atom, assumed to be in the ground state, cannot be excited, will be discussed. Rather than develop the general theory of elastic scattering of electrons by atoms the simple example of electron scattering by the ground state of hydrogen will be studied at first, and the results for some other atoms discussed later.

The mass of the electron can be neglected in comparison with the mass of the nucleus of the atom, so that the laboratory and center of mass systems coincide and the nucleus may be taken as the origin of the coordinate system. In atomic units, the Schrödinger equation of a system of two electrons and a proton is

$$\mathbf{L}\Psi = \left[-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} - E \right] \Psi(\mathbf{r}_1, \mathbf{r}_2) = 0,$$

(5-1)

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the position vectors of electrons 1 and 2, with respect to the proton. The interactions are purely coulombic since for light atoms spin dependent potentials, such as the spin orbit potential $(\mathbf{L} \cdot \mathbf{S})$ are very small and may be neglected. The total spin of the system is then conserved, and in the present case, as each electron has spin one-half, the total

spin S of the two electron system[1] is given by $S^2 = s(s + 1)\hbar^2$ with $s = 0$ or $s = 1$. The state with $s = 0$ is a singlet state and the corresponding spin wave function, χ_{sm} where $m\hbar$ is the Z component of the spin, is

$$\chi_{0,0} = \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \alpha(2)\beta(1)], \qquad (5-2)$$

where $\alpha(i)$ is the spin wave function of electron i, quantized parallel to the Z axis, $(m = 1/2)$ and $\beta(i)$ is the spin wave function quantized anti-parallel to the Z axis, $(m = -1/2)$.

The state with $s = 1$ is a triplet state and

$$\chi_{1,1} = \alpha(1)\alpha(2),$$

$$\chi_{1,0} = \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \beta(1)\alpha(2)],$$

$$\chi_{1,-1} = \beta(1)\beta(2). \qquad (5-3)$$

The singlet state is antisymmetrical under the interchange of electrons 1 and 2, while the triplet state is symmetrical.

The Pauli principle states that the wave function of a system of identical particles of spin one-half must be completely antisymmetrical, and it follows that the spatial part of the wave function $\psi^S(r_1, r_2)$ must be symmetrical for the singlet state $s = 0$ and antisymmetrical for the triplet states $s = 1$

$$\psi^S(r_1, r_2) = (-1)^S \psi^S(r_2, r_1). \qquad (5-4)$$

Because the Schrödinger equation (5-1) is symmetrical in 1 and 2, the solutions divide into a symmetrical and an antisymmetrical class and this would remain true even in the absence of the Pauli principle. The symmetry is a constant of the motion and the symmetrical and antisymmetrical wave functions are orthogonal.

Boundary conditions

If the incident electron has a kinetic energy less than

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[1] To a high degree of approximation the electron spins do not interact with the spin of the nucleus, and only the electron spins need be considered.

10.2 ev the hydrogen atom cannot be excited, and at large distances of separation the wave function must become equal to the product of a free electron wave function and the target atom wave function. If electron 1 is incident on the atom we have

$$\Psi^S(\mathbf{r_1},\mathbf{r_2}) \xrightarrow[r_1 \to \infty]{} \mathfrak{F}^S(\mathbf{r_1})\varphi_0(r_2), \tag{5-5}$$

where $\varphi_0(r_2)$ is the normalized ground state wave function of hydrogen. The hydrogenic wave functions $\varphi_n(\mathbf{r_2})$ satisfy

$$(-1/2\nabla_2^2 - 1/r_2 - \epsilon_n)\varphi_n(\mathbf{r_2}) = 0, \tag{5-6}$$

where ϵ_0 is the ground state energy.

The free electron wave function must satisfy the incoming plane wave and outgoing spherical wave boundary conditions discussed in Chapter 1, so we can take $\mathfrak{F}^S(\mathbf{r_1})$ to be

$$\mathfrak{F}^S(\mathbf{r_1}) = \exp(i\mathbf{k_0} \cdot \mathbf{r_1}) + r_1^{-1}f^S(\theta)e^{ik_0r}, \tag{5-7}$$

where $f^S(\theta)$ is the scattering amplitude and $\mathbf{k_0}$ is the momentum of the incident electron. We have (in atomic units)

$$E = \frac{1}{2}k_0^2 + \epsilon_0 = \frac{1}{2}(k_0^2 - 1).$$

Because of the symmetry properties of the solution, the boundary conditions for large r_2 must be

$$\Psi^S(\mathbf{r_1},\mathbf{r_2}) \xrightarrow[r_2 \to \infty]{} (-1)^S\mathfrak{F}^S(\mathbf{r_2})\varphi_0(r_1). \tag{5-8}$$

It is of course perfectly possible to discuss solutions which are not symmetrical and which are linear combinations of Ψ^0 and Ψ^1, but the possibility of electron "exchange", in which electron 1 is captured and electron 2 becomes free, must be included in the boundary conditions.

The differential cross sections for scattering when the electron-hydrogen atom system is in an eigenstate of spin is $\left|f^S(\theta)\right|^2$. In an unpolarised beam of electrons there will be three times as many electrons in the triplet state $(s = 1)$ as in the singlet state $(s = 0)$, so the differential cross section for scattering of an unpolarised beam is obtained by summing over the final and averaging over the initial spin states.

$$\frac{d\sigma}{d\Omega} = \frac{3}{4} |f^1(\theta)|^2 + \frac{1}{4} |f^0(\theta)|^2 \ . \tag{5-9a}$$

The total cross section is then

$$\sigma = \frac{\pi}{2} \int_{-1}^{+1} d(\cos\theta) [3 |f^1(\theta)|^2 + |f^0(\theta)|^2] . \tag{5-9b}$$

The variational method

The Kohn-Hulthén variational method for the scattering amplitude described for potential scattering is easily generalized to the present case. Two solutions of the Schrödinger equation are defined, Ψ_1^S and Ψ_2^S where (omitting the superscript s),

$$\Psi_1(\mathbf{r}_1, \mathbf{r}_2) = \Psi_{\mathbf{k}_0}^{+}(\mathbf{r}_1, \mathbf{r}_2) \underset{r_1 \to \infty}{\sim} \left[\exp(i\mathbf{k}_0 \cdot \mathbf{r}_1) + \right.$$

$$\left. + r^{-1} f_{\mathbf{k}_0}^{+}(\theta) \frac{e^{ik_0 r_1}}{r_1} \right] \varphi_0(r_2) \tag{5-10a}$$

$$\Psi_2(\mathbf{r}_1, \mathbf{r}_2) = \Psi_{\mathbf{k}}^{-}(\mathbf{r}_1, \mathbf{r}_2) \underset{r_1 \to \infty}{\sim} \left[\exp(i\mathbf{k} \cdot \mathbf{r}_1) + \right.$$

$$\left. + r^{-1} f_{\mathbf{k}}^{-}(\theta) \frac{e^{-ikr_1}}{r_1} \right] \varphi_0(r_2) . \tag{5-10b}$$

Following the arguments given in section 2-1 and defining $I[\Psi_1, \Psi_2]$ as

$$I[\Psi_1, \Psi_2] = -2(\Psi_2, \mathbf{L}\Psi_1) , \tag{5-11}$$

where, in the usual notation,

$$(\Psi_1, \mathbf{L}\Psi_2) = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \ \Psi_1^*(\mathbf{r}_1, \mathbf{r}_2) \ \mathbf{L}\Psi_2(\mathbf{r}_1, \mathbf{r}_2)$$

and where $\mathbf{L}$ is given by (5-1), it is found that

$$\Delta I = I[\bar{\Psi}_1, \bar{\Psi}_2] = -4\pi\Delta f_{\mathbf{k}_0}^{+}(\theta) + I[\Delta\Psi_1, \Delta\Psi_2] . \tag{5-12}$$

Here $\bar{\Psi}_1$ and $\bar{\Psi}_2$ are trial functions which satisfy boundary conditions of the same form as Ψ_1 and Ψ_2, but with scattering amplitudes $(f^+ + \Delta f^+)$ and $(f^- + \Delta f^-)$, rather than f^+ and f^-.

The error in f_{k_0} will be of second order if the condition that $\Delta I = 0$ is satisfied with suitable trial functions.

A simple trial function for Ψ_i^S is

$$\overline{\Psi}_i^S(r_1, r_2) = F_i^S(r_1)\varphi_0(r_2) + (-1)^S F_i^S(r_2)\varphi_0(r_1), \quad i = 1,2.$$

$$(5-13)$$

The asymptotic forms of the functions F_i^S are then

$$F_1^S(r) \sim \exp(i\mathbf{k}_0 \cdot \mathbf{r}) + r^{-1}f_1^S(\theta)e^{ik_0 r},$$

$$F_2^S(r) \sim \exp(i\mathbf{k} \cdot \mathbf{r}) + r^{-1}f_2^S(\theta)e^{-ikr}.$$

Using the symmetry of the wave function, it is found that

$$\Delta I = I[\overline{\Psi}_1, \overline{\Psi}_2] = -4\int dr_1 \int dr_2 F_2^S(r_1)\varphi_0(r_2)L\left\{F_1^S(r_1)\varphi_0(r_2) + \right.$$

$$\left. + (-1)^S F_1^S(r_2)\varphi_0(r_1)\right\}.$$

$$(5-14)$$

Keeping in mind that F_2^S differs from the exact function (if the wave function is capable of being represented in this form) by a first order quantity which is arbitrary, the condition $I = 0$ is satisfied by the requirement

$$\int dr_2 \varphi_0(r_2) L\left\{F^S(r_1)\varphi_0(r_2) + (-1)^S F^S(r_2)\varphi_0(r_1)\right\} = 0,$$

$$(5-15)$$

where the subscript on F^S is now unnecessary and has been omitted.

The Schrödinger equation (5-6) satisfied by the hydrogen atom state wave φ_0 can be employed to reduce this equation for $F^S(r)$ to the form

$$(\nabla_1^2 + k_0^2)F^S(r_1) = U(r)F^S(r_1) + (-1)^S\int K(r_1, r_2)F^S(r_2)dr_2.$$

$$(5-16)$$

The potential $U(r)$ is defined by the equation

$$U(r) = -2\int\varphi_0^*(r_2)\left[\frac{1}{r_1} - \frac{1}{|r_1 - r_2|}\right]\varphi_0(r_2)dr_2,$$

$$(5-17)$$

Using Green's theorem it is straightforward to show that

$$\int d\,\mathbf{r}_2\varphi_0(\mathbf{r}_2)\mathbf{L}\varphi_0(\mathbf{r}_1)F^S(\mathbf{r}_2) = \int d\,\mathbf{r}_2 F^S(\mathbf{r}_2)\mathbf{L}\{\varphi_0(\mathbf{r}_1)\varphi_0(\mathbf{r}_2)\}.$$

From this result the non-local potential K is defined as

$$K(\mathbf{r}_1,\mathbf{r}_2) = 2\,\mathbf{L}\,\{\varphi_0(\mathbf{r}_1)\varphi_0(\mathbf{r}_2)\}$$

$$= -2\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2)\left[-\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}+(E-2\epsilon_0)\right]. \quad (5\text{-}18)$$

The potential $U(r)$ is the electron-atom interaction averaged over the ground state wave function, and the non-local potential[2] K describes electron exchange, in which the two electrons interchange. With this form of trial function, no allowance is made for the possible distortion of the hydrogen wave function during the collision and no explicit terms depending on $|\mathbf{r}_1-\mathbf{r}_2|$ describing correlations between the two electrons appear in the wave function. The importance of both these effects is expected to be enhanced at low energies, and we will see later how they may be taken into account.

To evaluate the integral in (5-17), it is convenient to use the expansion (Morse and Feshbach, 1953, p. 1274)

$$\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|} = \sum_{n=0}^{\infty}\gamma_n(\mathbf{r}_1,\mathbf{r}_2)P_n(\cos\theta_{12}), \quad (5\text{-}19)$$

where θ_{12} is the angle between $\mathbf{r}_1$ and $\mathbf{r}_2$, and

$$\gamma_n = \frac{1}{r_>}\left(\frac{r_<}{r_>}\right)^n, \quad (5\text{-}20)$$

$r_<, r_>$ being the lesser and greater or r_1 and r_2 respectively. The hydrogen ground state function is

$$\varphi_0(r) = \frac{1}{\sqrt{\pi}}\,e^{-r}$$

and performing the integral over r_2, we find

$$U(r) = -2(1+1/r)e^{-2r}. \quad (5\text{-}21)$$

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[2] It is possible to show that a non-local potential of this kind is equivalent to an ordinary potential which, however, is velocity dependent, containing operators such as $\mathbf{p} = -i\hbar\nabla$ (Mittleman, 1965).

To calculate the partial wave amplitudes and the corresponding phase shifts, the wave function $F^S(\mathbf{r})$ can be expanded in the usual way (section 1-2) as

$$F^S(\mathbf{r}) = \sum_{\ell} A_{\ell} r^{-1} f_{\ell}^S(r) P_{\ell}(\cos\theta),$$

where the A_{ℓ} are normalization constants.

In obtaining the radial equations, the Legendre polynomial expansion of K is required. Using (5-19) we find

$$K(\mathbf{r_1},\mathbf{r_2}) = \sum_{\ell=0}^{\infty} (r_1 r_2)^{-1} K_{\ell}(r_1,r_2) \left(\frac{2\ell+1}{4\pi}\right) P_{\ell}(\cos\theta_{12})$$

(5-22a)

with

$$K_{\ell}(r_1,r_2) = -\left(\frac{8r_1 r_2}{2\ell+1}\right) e^{-(r_1+r_2)} \left[(E-2\epsilon_0)\delta_{\ell,0} - \gamma_{\ell}(r_1,r_2)\right]$$

(5-22b)

Expressing $P_{\ell}(\cos\theta_{12})$ in terms of θ_1 and θ_2 by the addition theorem (Morse and Feshbach, 1953, p. 1274)

$$\sqrt{\frac{2\ell+1}{4\pi}} P_{\ell}(\cos\theta_{12}) = \sum_{m} Y_{\ell,m}(\theta_1,\varphi_1) Y_{\ell,-m}(\theta_2,\varphi_2),$$

(5-23)

the integration over angles in the kernel is effected. The required radial equation is then

$$\left(\frac{d^2}{dr_1^2} - \frac{\ell(\ell+1)}{r_1^2} + k_0^2\right) f_{\ell}^S(r_1) = U(r) f_{\ell}^S(r_1) +$$

$$+ (-1)^S \int_0^{\infty} K_{\ell}(r_1,r_2) f_{\ell}^S(r_2) dr_2,$$

(5-24)

which may be solved numerically with the boundary conditions

$$f_{\ell}^S(r) \sim s_{\ell}(k_0 r) + \tan\delta_{\ell}^S c_{\ell}(k_0 r).$$

(5-25)

The s wave phase shifts ($\ell=0$) in this approximation, which
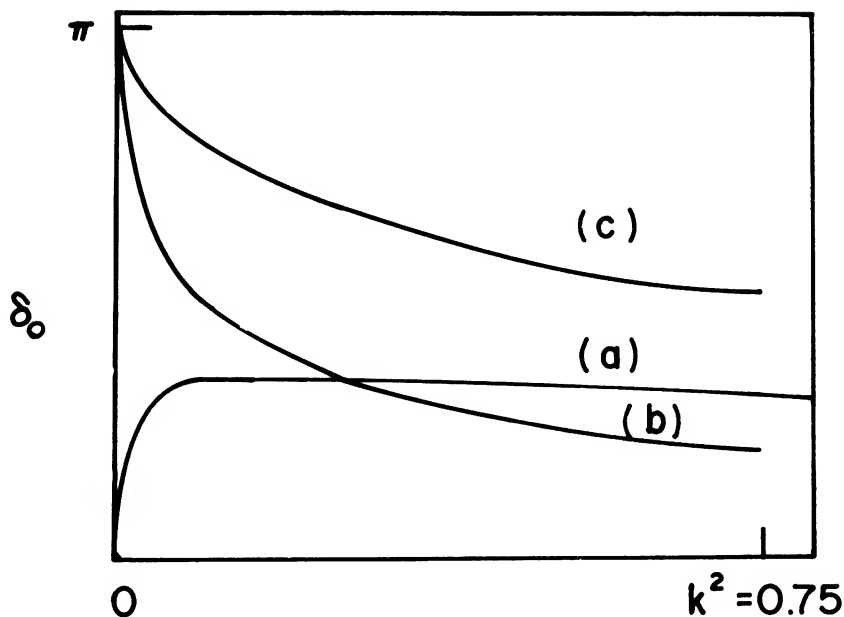
Figure 5-1. Phase shifts for the elastic scattering of electrons by hydrogen atoms, calculated (a) with no allowance made for exchange, (b) singlet phase shifts in the static exchange approximation, (c) triplet phase shifts in the static exchange approximation.

we shall call the static exchange approximation, are shown[3] in Fig. (5-1), together with the phase shifts when the exchange kernel K_0 is neglected. It can be seen at once that exchange is of great significance at low energies, the phase shifts δ_0^1 and δ_0^0 both tending to π as $k \to 0$, while the non-exchange phase shift $\delta_0 \to 0$ as $k \to 0$. These results illustrate the breakdown of Levinson's theorem for non-local potentials. For singlet scattering (s = 0) there exists one bound state with zero angular momentum of the system of two electrons and a proton. This is the hydrogen negative ion, with a binding energy of $\epsilon_{H^-} = -0.75$ ev. Levinson's theorem therefore

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[3] See John (1960). A collection of results and other references are given by Burke and Smith (1962).

applies in this case. For triplet scattering no such state exists and according to Levinson's theorem the phase shift δ_0^1 should tend to zero as $k_0 \to 0$. The failure of Levinson's theorem is due to the existence of a bounded solution of equation (5-24), which vanishes for large r and yet does not correspond to a bound state. That such a solution exists can be seen from equation (5-15), which is satisfied identically if we take

$$F^1(r) = \varphi_0(r). \tag{5-26}$$

Correspondingly equation (5-24) is solved, for $\ell = 0$, by setting

$$f_0^1(r) = r\varphi_0(r). \tag{5-27}$$

If $f_0^1(r)$ is any solution of (5-24) satisfying the boundary condition for scattering (5-25), then

$$f_0^1(r,\lambda) = f_0^1(r) + \lambda r \varphi_0(r), \tag{5-28}$$

is also an acceptable solution having the same phase shift, where λ is an arbitrary constant. This degeneracy can be removed, if desired, by requiring $f_0^1(r,\lambda)$ to be orthogonal to the ground state of hydrogen:

$$\int_0^\infty r\varphi_0(r)f_0^1(r,\lambda)dr = 0. \tag{5-29}$$

The existence of such a solution, vanishing at infinity, gives rise to an additional zero in the Jost function, $\varphi_0(-k)$, which in turn modifies the derivation of Levinson's theorem, so that now

$$\delta_0^1(0) - \delta_0^1(\infty) = \pi. \tag{5-30}$$

The location of the zero can be determined as follows. Using the orthogonality condition (5-29), equation (5-24) for $f_0^1(r)$ is modified by the omission of the part of the kernel K that contains $(E - 2\epsilon_0)$ as a factor (see 5-22b). It can then be verified that $r\varphi_0(r)$ is an eigenfunction of the modified equation belonging to the eigenvalue $k^2 = -1$. The corresponding zero in the Jost function occurs at $k = i$.

Martin (1955) (see also Swan, 1954) has shown, for kernels that vanish when r or r' exceeds a certain value r_0, that Levinson's theorem takes the form

$$\delta_\ell(0) - \delta_\ell(\infty) = (n + m)\pi, \tag{5-31}$$

where n is the number of bound states and m is the number of families of degenerate solutions vanishing at infinity. Physically these solutions are connected with bound states that could exist if they were not excluded by the Pauli principle.

The phase shifts for $\ell = 1$ and $\ell = 2$ in the static approximation are much smaller than those for $\ell = 0$. The total cross section does not depend significantly on either the $\ell = 1$ or $\ell = 2$ terms, but the angular distributions are modified by the $\ell = 1$ phase shifts and to a small extent by the $\ell = 2$ phase shifts, and show a departure from isotropy. Some results are shown in Table 5-1 for the $\ell = 0$, $\ell = 1$ and $\ell = 2$ phase shifts.

Table 5-1

Phase shifts for the scattering of electrons by hydrogen atoms in the static exchange approximation

| k^2 (a.u.) | Phase shifts in radians | | | | | |
| | Singlet (s = 0) | | | Triplet (s = 1) | | |
	$\ell = 0$	$\ell = 1$	$\ell = 2$	$\ell = 0$	$\ell = 1$	$\ell = 2$
0.0*	8.098	--	--	2.350	--	--
0.1	2.396	-0.0012	--	2.908	0.0022	--
0.3	0.9488	-0.0811	--	1.987	0.20000	--
0.5	0.7370	-0.1084	-0.0108	1.739	0.2866	0.0230
0.76	0.6087	-0.1159	-0.0155	1.541	0.3362	0.0395

* Scattering lengths are shown for $k^2 = 0$, in units of a_0.

5-2   ALTERNATIVE BOUNDARY CONDITIONS

The exact wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ may be expanded in a complete ortho-normal set of hydrogen atom eigenfunctions

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_n \varphi_n(\mathbf{r}_2) F_n(\mathbf{r}_1) + \int d\mathbf{K} \varphi_\mathbf{K}(\mathbf{r}_2) F(\mathbf{K}, \mathbf{r}_1) , \qquad (5-32)$$

where we have distinguished the bound hydrogenic functions φ_n from the continuum functions $\varphi_\mathbf{K}(\mathbf{r}_2)$. The functions

$\varphi_K(r_2)$ are Coulomb functions of the kind discussed in Chapter 3 and are eigenfunctions of energy with $\epsilon(K) = K^2/2$. The boundary conditions satisfied by the functions $F_n(r_1)$ and $F(K, r_1)$, when the incident energy is less than the first excitation threshold, are

$$F_0(r_1) \sim \exp(i k_0 \cdot r_1) + r_1^{-1} f_0(\theta) e^{i k_0 r_1}, \tag{5-33}$$

and

$$r_1 F_n(r_1) \xrightarrow[r_1 \to \infty]{} 0 \quad n \neq 0$$

$$r_1 F(K, r_1) \xrightarrow[r_1 \to \infty]{} 0. \tag{5-34}$$

The functions F_n describe the motion of an electron moving relative to a hydrogen atom in the state n, and the conditions (5-34) follow from the requirement that the flux of particles must vanish at large distances for all n, except $n = 0$. The solution Ψ is neither symmetrical nor antisymmetrical like the solutions Ψ^S but, having obtained Ψ, solutions of the correct symmetry $\Psi^S = [\Psi(r_1, r_2) + (-1)^S \Psi(r_2, r_1)]$ may be constructed. The possibility of rearrangement exists, independently of the symmetry of the solution, so that $\Psi(r_1, r_2)$ must obey the additional (and independent) boundary conditions

$$\int \varphi_n^*(r_1) \Psi(r_1, r_2) d r_1 = G_n(r_2),$$

$$\int \varphi_K^*(r_1) \Psi(r_1, r_2) d r_1 = G(K, r_2), \tag{5-35a}$$

where

$$G_0(r_2) \xrightarrow[r_2 \to \infty]{} r_2^{-1} g_0(\theta) e^{i k_0 r_2},$$

$$r_2 G_n(r_2) \xrightarrow[r_2 \to \infty]{} 0, \quad n \neq 0 \tag{5-35b}$$

$$r_2 G(K, r_2) \xrightarrow[r_2 \to \infty]{} 0.$$

It has been assumed that electron 1 is incident on the atom and therefore only outgoing waves are present in the rearranged state.

It is not immediately obvious how the boundary

conditions (5-35) can be satisfied by the expansion (5-32).
Clearly, each of the bound state terms $\varphi_n(r_2)$ in the sum
(5-32) vanishes for large $|r_2|$, and any non-zero contributions
to $\Psi(r_1, r_2)$ at large $|r_2|$ must come from the continuum terms
in the expansion[4]. Assuming the Coulomb potentials are
screened, to avoid logarithmic phase factors, the functions
$\varphi_K(r_2)$ have the asymptotic form

$$\varphi_K(r_2) \sim \exp(i\mathbf{K} \cdot r_2) + r_2^{-1} h_K(\theta)\exp(iKr_2),$$

where $h_K(\theta)$ is a scattering amplitude. From the oscillating
character of these functions, it follows that as

$$\Psi(r_1, r_2) \underset{r_2 \to \infty}{\sim} \int d\mathbf{K}\varphi_K(r_2)F(\mathbf{K}, r_1), \qquad (5-36)$$

$\Psi(r_1, r_2)$ must vanish for large r_2, unless $F(\mathbf{K}, r_1)$ is a singular
function of $\mathbf{K}$. To see that this function is singular, $F(\mathbf{K}, r_1)$ can
be expanded in the set of eigenfunctions $\{\varphi_n(r_1), \varphi_K(r_1)\}$:—

$$F(\mathbf{K}, r_1) = \sum_n a(\mathbf{K}, n)\varphi_n(r_1) + \int d\mathbf{K}' a(\mathbf{K}, \mathbf{K}')\varphi_{K'}(r_1). \, (5-37)$$

The coefficients $a(\mathbf{K}, n)$ can be obtained from the equation

$$\int d r_1 \int d r_2 \left[\varphi_K^*(r_2)\varphi_n^*(r_1) L \Psi(r_1, r_2) \right] = 0,$$

using expansions (5-32) and (5-37) for $\Psi(r_1, r_2)$. The coeffi-
cients $a(\mathbf{K}, \mathbf{K}')$ can be found in the same way. On using the
Schrödinger equations satisfied by the ortho-normal hydrogenic
functions, (5-6), it is easy to show that

$$a(\mathbf{K}, n) = \left(E - \epsilon_n - \frac{1}{2}K^2 \right)^{-1} A(\mathbf{K}, n), \qquad (5-38)$$

and

$$A(\mathbf{K}, n) = \int d r_1' \int d r_2' \, \varphi_K(r_2')\varphi_n(r_1')V(|r_1' - r_2'|)\Psi(r_1', r_2').$$

$$(5-39)$$

In this expression $V(r)$ is the screened Coulomb potential and

4
Castillejo et al. (1960).

for such a potential $A(\mathbf{K}, n)$ is a well behaved function of $\mathbf{K}$.
Similar expressions can be written down for $A(\mathbf{K}, \mathbf{K}')$.

The coefficient $A(\mathbf{K}, n)$ and hence $F(\mathbf{K}, \mathbf{r}_1)$ is
singular if the denominator in (5-38) vanishes, that is when

$$E = \epsilon_n + \frac{1}{2}K^2.$$

When the total energy $E = (\epsilon_0 + k_0^2/2)$ is below the first
excitation threshold, this can happen only when $n = 0$, and
$K^2 = k_0^2$, and the coefficient $a(\mathbf{K}, \mathbf{K}')$ is non-singular, in this
interval.

The non-vanishing part of $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ at large r_2, is
then obtained from the term $a(\mathbf{K}, 0)$, and using (5-39) and
(5-36), we find

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) \underset{r_2 \to \infty}{\sim} \left[\int d\mathbf{K} \varphi_{\mathbf{K}}(\mathbf{r}_2) \frac{A(\mathbf{K}, 0)}{(E - \epsilon_0 - K^2/2)} \right] \varphi_0(\mathbf{r}_1).$$

$$(5\text{-}40)$$

The integral over $\mathbf{K}$ is of the form

$$\int d\mathbf{K} \frac{\varphi_{\mathbf{K}}(\mathbf{r}_2) \varphi_{\mathbf{K}}^*(\mathbf{r}_2')}{(k_0^2 - K^2)}$$

and is similar to that occurring in the discussion of Green's
functions in Chapter 1. It can be evaluated by adding $i\epsilon$ to
k_0^2 and by using Cauchy's integral theorem, and the results
(5-35) can then be established. It is found that

$$\int d\mathbf{K} \frac{\varphi_{\mathbf{K}}(\mathbf{r}_2) \varphi_{\mathbf{K}}^*(\mathbf{r}_2')}{(k_0^2 - K^2)} \xrightarrow[r_2 \to \infty]{} - \frac{e^{ik_0 r_2}}{2\pi r_2} \varphi_{-\mathbf{k}}^*(\mathbf{r}_2'), \qquad (5\text{-}41)$$

where $\mathbf{k}$ is a vector in the direction of $\mathbf{r}_2$ and $|k| = |k_0|$ so
that

$$g_0(\theta) = - \frac{1}{2\pi} \int d\mathbf{r}_1' \int d\mathbf{r}_2' \varphi_{-\mathbf{k}}^*(\mathbf{r}_2') \varphi_0(\mathbf{r}_1') V(|\mathbf{r}_1' - \mathbf{r}_2'|) \Psi(\mathbf{r}_1', \mathbf{r}_2').$$

$$(5\text{-}42)$$

Details of the calculation are given by Castillejo et al. (1960)
These results are already contained in the general theory estab-
lished in Chapter 4, but it is instructive to see how the asymp-
totic conditions are satisfied in this explicit manner.

The expansion (5-32) with the boundary conditions (5-33, 5-34) is unique, but alternative expansions such as

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_n \varphi_n(\mathbf{r}_2) F_n(\mathbf{r}_1) + \sum_n \varphi_n(\mathbf{r}_1) G_n(\mathbf{r}_2), \qquad (5-43)$$

are clearly not so. (Here we have reverted to our usual practice, in which the sum over n includes an integration over the continuum.) This freedom allows us to choose the F_n and G_n functions to be non-singular in n, so that for large $|\mathbf{r}_1|$, only the first sum contributes to the boundary conditions (5-33) and for large $|\mathbf{r}_2|$ only the second sum contributes to the rearranged boundary conditions (5-35). These remarks are not confined to low energies below the excitation threshold, but can be generalised appropriately.

To calculate the cross sections from the amplitudes $f_0(\theta)$ and $g_0(\theta)$ introduced in (5-33) and (5-35b) the solutions of definite symmetry Ψ^S are formed. Using the asymptotic forms of these solutions, we find at once that

$$f^S(\theta) = f_0(\theta) + (-1)^S g_0(\theta), \qquad (5-44)$$

and the differential cross section for an unpolarized beam becomes

$$\frac{d\sigma}{d\Omega} = |f_0(\theta)|^2 + |g_0(\theta)|^2 - \text{Re}\left[f_0(\theta) g_0^*(\theta)\right]. \qquad (5-45)$$

The first two terms may be considered as giving the intensities of direct and rearranged scattering, while the last term represents interference which is specifically related to the identity of the electrons and is due to the Pauli exclusion principle.

5-3   THE LONG RANGE INTERACTION AND THE POLARIZED ORBITAL METHOD

The trial function (5-13) in the static exchange method does not include terms representing the distortion or polarization of the target atom by the field of the incident electron. This distortion gives rise to an interaction between the electron and the atom that, at energies below the first inelastic threshold, varies like $(1/r^4)$ and is characteristic of the interaction between a

charged particle and a neutral polarizable system.[5] To iden-
tify the long range potential (Castillejo et al., 1960) the
expansion of the total wave function (5-32) is inserted in the
Schrödinger equation to obtain an infinite set of coupled equa-
tions for the functions $F_n(\mathbf{r}_1)$

$$\int \varphi_n^*(\mathbf{r}_2) L\left[\sum_m \varphi_m(\mathbf{r}_2) F_m(\mathbf{r}_1)\right] d\mathbf{r}_2 = 0, \quad n = 0,1,2 \ldots .$$

Using the wave equation (5-6) for the hydrogenic functions
$\varphi_m(\mathbf{r}_2)$, we find

$$(\nabla^2 + k_n^2) F_n(\mathbf{r}_1) = \sum_{m=0}^{\infty} V_{nm}(\mathbf{r}_1) F_m(\mathbf{r}_1), \tag{5-46}$$

where

$$k_n^2 = k_0^2 + 2\epsilon_0 - 2\epsilon_n,$$

and

$$V_{nm} = 2\int \varphi_n^*(\mathbf{r}_2) \left(\frac{1}{r_{12}} - \frac{1}{r_1}\right) \varphi_m(\mathbf{r}_2) d\mathbf{r}_2. \tag{5-47}$$

For $n \neq 0$, k_n^2 is negative since the corresponding channel is
closed. Using the expansion (5-19) for $1/r_{12}$, the form
of V_{nm} for large r_1 may be determined.

Consider the potential V_{0m} which connects the equa-
tion for F_0 (the wave function in the open channel) with the
closed channel wave functions. The bound hydrogenic func-
tions $\varphi_m(\mathbf{r}_2)$ are eigenfunctions of angular momentum of the
form

$$\varphi_m(\mathbf{r}_2) = r_2^{-1} R_{n\ell}(r_2) P_\ell(\cos \theta_2). \tag{5-48}$$

Here m stands collectively for the usual orbital and principal
quantum numbers ℓ and n, and $R_{n\ell}$ is the radial wave func-
tion. Only the ℓth term in the Legendre polynomial expansion
of $1/r_{12}$ will contribute to V_{0m}, from which we see that

$$V_{0m}(\mathbf{r_1}) \propto 1/r_1^{\ell+1} \quad \text{for large } r_1 \ (\ell \neq 0), \tag{5-49}$$

when $\ell = 0$, $V_{0m}(\mathbf{r_1})$ vanishes exponentially as $r_1 \to \infty$. It follows that the dominant terms for large r_1 arise from p states ($\ell = 1$) and for these $V_{0m} \propto 1/r_1^2$. Castillejo et al. were able to show that for all states n and m (including continuum states) $V_{nm}(\mathbf{r_1})$ decreases at least as fast as $1/r_1^2$ as $r_1 \to \infty$. In view of the boundary condition (5-34), for large r_1 and $n \neq 0$ the only term of importance on the right hand side of each of the equations (5-46) is that connecting the channel n with the open channel 0; hence

$$(\nabla^2 + k_n^2)F_n(\mathbf{r_1}) \simeq V_{n0}(\mathbf{r_1})F_0(\mathbf{r_1}), \ r_1 \text{ large}. \tag{5-50}$$

For large r_1, we must have that

$$\nabla^2 F_0(\mathbf{r_1}) = -k_0^2 F_0(\mathbf{r_1}) + 0\left(\frac{1}{r_1^4}\right), \tag{5-51}$$

and if $V_{n0}(\mathbf{r_1}) \propto (1/r_1)^p$, with $p \geq 2$, we have

$$\nabla^2\left[V_{n0}(\mathbf{r_1})F_0(\mathbf{r_1})\right] = -k_0^2\left[V_{n0}(\mathbf{r_1})F_0(\mathbf{r_1})\right] + 0\left(\frac{1}{r_1^{p+1}}\right), \tag{5-52}$$

Comparing this relation with equation (5-50), we see that the functions $F_n(\mathbf{r_1})$ have the form, for large r_1,

$$F_n(\mathbf{r_1}) \sim \frac{1}{k_n^2 - k_0^2} V_{n0}(\mathbf{r_1})F_0(\mathbf{r_1}); \quad n \neq 0. \tag{5-53}$$

By substituting this expression for F_n into equation (5-46), the equation satisfied by $F_0(\mathbf{r})$ for large r, is found to be

$$(\nabla^2 + k_0^2)F_0(\mathbf{r}) = U(r)F_0(\mathbf{r}) + U_p(r)F_0(\mathbf{r}), \tag{5-54}$$

where

$$U_p(r) = \sum_{n \neq 0} \frac{|V_{0n}(\mathbf{r_1})|^2}{(k_n^2 - k_0^2)}, \tag{5-55}$$

and U(r) is defined by (5-21). As the dominant (p wave) terms in V_{0n} vary as $1/r^2$ for large r, the polarization

potential $U_p(r)$ varies as $1/r^4$ as $r \to \infty$ and this is the exact long range potential, up to terms of $0(1/r^6)$. The polarization is attractive because the denominator in (5-55) is always negative.

Adiabatic polarization

When a hydrogen atom is placed in the field of a fixed charge, it is distorted or 'polarized' and the energy levels will be shifted. The new energy and wave function can be calculated by perturbation theory. The approximation in which it is assumed that the electron is moving so slowly that its kinetic energy may be neglected is known as the adiabatic approximation and we shall now show that the potential $U_p(r)$ is identical with the polarization energy calculated to second order in the adiabatic approximation. The Schrödinger equation for a hydrogen atom in the field of an electron fixed at position $\mathbf{r}$ is

$$[H_0 + \lambda V]\Phi(\mathbf{r},\mathbf{x}) = E(\mathbf{r})\Phi(\mathbf{r},\mathbf{x}), \qquad (5\text{-}56)$$

where

$$H_0 = \left(-\frac{1}{2}\nabla_x^2 - \frac{1}{x}\right); \quad V = \left(\frac{1}{|\mathbf{r} - \mathbf{x}|} - \frac{1}{r}\right), \qquad (5\text{-}57)$$

and $\lambda = 1$. Applying the ordinary Rayleigh-Schrödinger perturbation theory (see, for example, Landau and Lifschitz, 1958, p. 133), E and Φ are expanded in powers of λ

$$\Phi = \varphi_0(\mathbf{x}) + \lambda\varphi_{pol} + 0(\lambda^2),$$

$$\qquad (5\text{-}58)$$

$$E = E_0^{\,0} + \lambda E_0^{\,1} + \lambda^2 E_0^{\,2} + \ldots .$$

If the perturbation is removed by letting $\lambda \to 0$ the solution is required to coincide with the hydrogen ground state $\varphi_0(x)$ with energy $E_0^{\,0} = \epsilon_0$. The first order energy $E_0^{\,1}$ is ($\lambda = 1$),

$$E_0^{\,1}(r) = \int\varphi_0(\mathbf{x})V\varphi_0(\mathbf{x})d\mathbf{x}. \qquad (5\text{-}59)$$

It is seen that $2E_0^{\,1} = U(r)$, where $U(r)$ is the static interaction occurring in the scattering equation (5-16). The first order wave function $\varphi_{pol}(\mathbf{r},\mathbf{x})$ is given by ($\lambda = 1$)

$$\varphi_{pol}(\mathbf{r},\mathbf{x}) = \sum_{n \neq 0} \frac{\int\varphi_0(\mathbf{x})V\varphi_n^*(\mathbf{x})d\mathbf{x}}{(\epsilon_0 - \epsilon_n)} \varphi_n(\mathbf{x}), \qquad (5\text{-}60a)$$

and is the solution of the equation

$$(H_0 - \epsilon_0)\varphi_{pol} = E_0^1 \varphi_0(\mathbf{x}) - V\varphi_0(\mathbf{x}). \tag{5-60b}$$

The second order energy E_0^2 can be calculated from φ_{pol} and is given by

$$E_0^2 = \int \varphi_0(\mathbf{x})[V - E_0^1]\varphi_{pol}(\mathbf{r},\mathbf{x})d\mathbf{x} \tag{5-61}$$

$$= \sum_{n \neq 0} \frac{|\int \varphi_0(\mathbf{x})V\varphi_n(\mathbf{x})d\mathbf{x}|^2}{(\epsilon_0 - \epsilon_n)}.$$

Comparing (5-61) and (5-55) it is seen that $U_p(r) = 2E_0^2(r)$.

The interaction potential can be expanded in a multipole expansion

$$V(\mathbf{r},\mathbf{x}) = \sum_{\ell=0}^{\infty} V_\ell(r,x)P_\ell(\cos\theta), \tag{5-62a}$$

where

$$V_\ell(r,x) = \left[\gamma_\ell(r,x) - \delta_{\ell,0}\frac{1}{r}\right],$$

and θ is the angle between $\mathbf{x}$ and $\mathbf{r}$. The polarization potential U_p can also be expanded

$$U_p(r) = \sum_{\ell=0}^{\infty} U_p(\ell,r), \tag{5-62b}$$

where $U_p(\ell,r)$ is determined by the multipole of order ℓ.

$$U_p(\ell,r) = \sum_{n \neq 0} \frac{2|\int \varphi_0(\mathbf{x})V_\ell(r,x)P_\ell(\cos\theta)\varphi_n(\mathbf{x})d\mathbf{x}|^2}{(\epsilon_0 - \epsilon_n)}. \tag{5-62c}$$

As we noted earlier the multipole of longest range is the dipole term. This arises from the p states of hydrogen and

$$U_p \sim -\frac{a_1}{r^4}.$$

where a_1 is the dipole polarizability of the atom; for hydrogen,

$a_1 = 4.5$. The monopole contribution to U_p vanishes exponentially, while for $\ell \neq 0$

$$U_p(\ell, r) \sim -a_\ell / r^{2\ell+2}, \quad \text{as } r \to \infty, \tag{5-63a}$$

where

$$a_\ell = \sum_{n \neq 0} \frac{2 \left| \int \varphi_0(\mathbf{x}) \varphi_n(\mathbf{x}) x^\ell P_\ell(\cos \theta) d\mathbf{x} \right|^2}{(\epsilon_0 - \epsilon_n)} . \tag{5-63b}$$

In the case of hydrogen, exact solutions of (5-60b) and (5-61) have been obtained (Dalgarno and Lynn, 1957), and the multipole contributions to U_p and φ_{pol} for $\ell = 0, 1, 2$, have been calculated by Reeh (1960).

Corrections to the effective potential U_p, to be employed in equation (5-54) for $F_0(\mathbf{r})$, arise both from higher order terms in the perturbation series (5-58), and also by avoiding the adiabatic approximation, in which the kinetic energy of the electron is neglected. The leading non-adiabatic terms for large r, have been investigated by Kleinman et al. (1968) and by Dalgarno et al. (1968). Working to lowest order in the kinetic energy, the correction of the effective potential is easily seen to be of the form

$$\overline{U}(r) = \int d\mathbf{x} \, \Phi(\mathbf{r}, \mathbf{x}) \nabla_r^2 \Phi(\mathbf{r}, \mathbf{x}),$$

where Φ is the solution of equation (5-56). For large r, the leading term in $\overline{U}(r)$ is proportional to $(1/r^6)$. The only other term of this order arises from the quadrupole term $U_p(2, r)$ in the expansion of the adiabatic potential, and the exact asymptotic form of the effective potential up to terms of order $(1/r^7)$ is

$$U_p(r) \sim -\frac{a_1}{r^4} - (a_2 - 6\beta_1) \frac{1}{r^6} + 0\left(\frac{1}{r^7}\right), \tag{5-64}$$

where a_2 is the quadrupole polarizability. The coefficient β_1 is obtained from the expansion of $\overline{U}(r)$, and can be expressed in the form

$$\beta_1 = \sum_{n \neq 0} \frac{\left| \int \varphi_0(\mathbf{x}) x \cos \theta \, \omega_n(\mathbf{x}) d\mathbf{x} \right|^2}{(\epsilon_0 - \epsilon_n)^2} . \qquad (5\text{-}65)$$

In the case of hydrogen $\alpha_2 = 15$ and $\beta_1 = 5.375$, so that the non-adiabatic term has a significant effect in decreasing the effective attraction from that derived from the adiabatic approximation.

The method of polarized orbitals

The method of polarized orbitals (Temkin, 1957, 1960; Temkin and Lamkin, 1961) attempts to include both the effects of polarization and those of exchange (which are, as we saw earlier, of great importance), in a relatively simple approximation. The trial function Ψ_t is written in the form

$$\Psi_t^S(\mathbf{r}, \mathbf{x}) = \left[1 + (-1)^S P_{12} \right] \left[\varphi_0(\mathbf{x}) + \varphi_{pol}(\mathbf{x}, \mathbf{r}) \right] F^S(\mathbf{r}) , \qquad (5\text{-}66)$$

where P_{12} is an operator interchanging the coordinates of the two electrons. An equation for $F^S(\mathbf{r})$ is obtained by requiring

$$\int \varphi_0(\mathbf{x}) [H - E] \Psi_t^S(\mathbf{r}, \mathbf{x}) d\mathbf{x} = 0 . \qquad (5\text{-}67)$$

The equation for $F^S(\mathbf{r})$ is similar in form to (5-16):

$$[\nabla^2 + k^2 - U(r) - U_p(r)] F^S(\mathbf{r}) = \int \{ K(\mathbf{r}, \mathbf{r}') + K_p(\mathbf{r}, \mathbf{r}') \} F^S(\mathbf{r}') d\mathbf{r}' , \qquad (5\text{-}68)$$

where K_p is an additional kernel arising from the rearranged or exchange part of the wave function

$$K_p(\mathbf{r}, \mathbf{r}') = (-1)^S 2 \varphi_0(\mathbf{r}') [H - E] \varphi_{pol}(\mathbf{r}, \mathbf{r}') . \qquad (5\text{-}69)$$

The equation for $F^S(\mathbf{r})$ can be reduced to a set of radial equations by expanding in eigenfunctions of angular momentum in the usual way.

Since the wave function $\varphi_{pol}(\mathbf{r}, \mathbf{x})$ given by (5-60b) is certainly in error for small r, Temkin and Lamkin (1961) employed a simplified form, in which only the dipole contribution

was retained. In addition they required $\varphi_{pol}(\mathbf{r},\mathbf{x})$ to vanish when $r < x$. Thus φ_{pol} was of the form

$$\varphi_{pol}(\mathbf{r},\mathbf{x}) = \theta(r - x)r^{-1}f_p(r,x)\cos\theta, \qquad (5\text{-}70)$$

where $\cos\theta = \mathbf{r}\cdot\mathbf{x}/rx$ and $\theta(y) = 1$, $y > 0$, $\theta = 0$ otherwise. By substituting this form into equation (5-60b), f_p is found to satisfy

$$\left(\frac{d^2}{dx^2} - \frac{2}{x^2} + \frac{2}{x} - 1\right)f_p(r,x) = \frac{2}{\sqrt{\pi}}\frac{x^2}{r^2}e^{-x}, \qquad (5\text{-}71)$$

with the solution (Sternheimer, 1954)

$$f_p(r,x) = -\frac{1}{\sqrt{\pi}}\frac{x^2}{r^2}\left(1 + \frac{1}{2}x\right)e^{-x}. \qquad (5\text{-}72)$$

This gives the terms of longest range (which are proportional to $(1/r^2)$) correctly, and the corresponding form for U_p is

$$U_p(r) = -r^{-4}\left[\frac{9}{2} - \frac{2}{3}e^{-2r}\left(r^5 + \frac{9}{2}r^4 + 9r^3 + \frac{27}{2}r^2 + \frac{27}{2}r + \frac{27}{4}\right)\right].$$
$$(5\text{-}73)$$

This approximation for U_p is quite close to the exact dipole contribution $U_p(1,r)$. It vanishes at the origin and behaves like $(-a_1/r^4)$ for large r. In forming the exchange kernel some care has to be taken with terms involving the derivatives of the step function θ in (5-70). This has been investigated by Sloan (1964).

The modification of the phase shifts produced by the exchange kernel K_p is quite small. If K_p is omitted, a variation of the method is obtained that is known as the 'exchange-adiabatic' approximation. Several refinements of the polarized orbital method have been developed, and these will be examined a little later on.

The phase shifts found from the polarized orbital method are shown in Tables 5-2 and 5-3. The relative change in higher order phase shifts from the values given by the exchange equations is greater than for the $\ell = 0$ phase shift, as would be expected. Also included in the tables are the phase shifts given by Schwartz (1961) and Armstead (1968), which, as we shall see, may be considered to be 'exact', and comparison shows that the agreement in the case of the s-wave is very good.

Table 5-2

Singlet (s = 0) phase shifts for the elastic scattering of electrons by hydrogen atoms in the ground state

k(a.u.)	Phase shifts in radians $\ell = 0$			$\ell = 1$			$\ell = 2$		
	Ex.	P.O.	V	Ex.	P.O.	V	Ex.	P.O.	V
0*	8.10	5.7	5.95	--	--	--	--	--	--
0.1	2.396	2.853	2.553	-0.0012	0.0048	0.007	--	--	--
0.2	1.870	2.114	2.067	--	--	0.0147	--	--	--
0.3	1.568	1.750	1.696	-0.0241	0.0322	0.0170	0.0006	0.0113	--
0.4	1.239	1.469	1.415	--	--	0.0100	--	--	--
0.5	1.031	1.251	1.202	-0.0713	0.0392	-0.0007	-0.00397	0.266	--
0.75	0.694	0.904	--	-0.1126	0.0347	--	-0.0123	0.0456	--

* Scattering lengths.

Ex. = static exchange; P.O. = polarized orbital; V = Schwartz ($\ell = 0$); Armstead ($\ell = 1$).

Table 5-3

Triplet (s = 1) phase shifts for the elastic scattering of electrons by hydrogen atoms in the ground state

Phase shifts in radians

k(a.u.)	$\ell = 0$			$\ell = 1$			$\ell = 2$		
	Ex.	P.O.	V	Ex.	P.O.	V	Ex.	P.O.	V
0*	2.35	1.7	1.77	--	--	--	--	--	--
0.1	2.907	2.946	2.939	0.0021	0.0090	0.1140	--	--	--
0.2	2.679	2.732	2.717	--	--	0.0450	--	--	--
0.3	2.461	2.519	2.500	0.0511	0.098	0.1063	0.0008	0.0118	--
0.4	2.257	2.320	2.294	--	--	0.1873	--	--	--
0.5	2.070	2.133	2.105	0.169	0.245	0.2699	0.0070	0.0350	--
0.75	1.679	1.745	--	0.304	0.390	--	0.0274	0.0746	--

*Scattering lengths.

Ex. = static exchange; P.O. = polarized orbital; V = Schwarz $(\ell = 0)$; Armstead $(\ell = 1)$.

Comparison with experiment

There is little doubt that, up to energies close to the first inelastic threshold, the main physical mechanisms are well represented by the combination of the static interaction U with the polarization potential U_p and the exchange kernel. This may be verified by comparison with the experimental measurements. The total cross sections (Fig. 5-2) have been measured by Brackmann et al. (1958) and Neynaber et al. (1961). The measurements are quite consistent with the theoretical predictions of the polarized orbital method. The differential cross sections have been measured over a limited angular range (30° to 120°) by Gilbody et al. (1961) and also agree with theory, but the measurements are not sufficiently precise to determine accurately the phases for $\ell > 0$, which are the ones most likely to be in error.
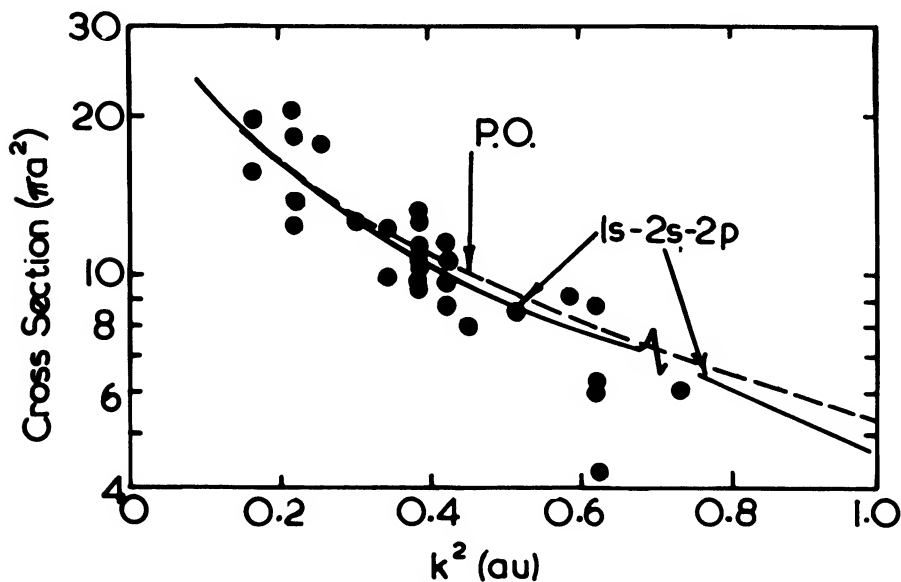
Figure 5-2.   The total elastic cross section for electron scattering by hydrogen atoms. The experimental points are due to Brackman et al. (1958) and to Neynaber et al. (1961). The calculated cross section in the 1s - 2s - 2p close coupling approximation is due to Burke and Schey (1962) and in the polarised orbital approximation to Temkin and Lamkin (1961).

5-4   FURTHER VARIATIONAL CALCULATIONS AND THE CLOSE COUPLING METHOD

Much more elaborate trial functions than the simple function (5-13), which gave the static exchange approximation, may be devised. These may be classified as purely algebraical, of close coupling (or eigenfunction expansion) form or as a mixture of the two. Each case will be considered in turn.

Algebraic trial functions

The Kohn or Hulthén variational methods may be employed with trial functions that depend on a number of parameters including the phase shifts. For example, if the trial function for s-wave scattering is written in the form

$$\Psi_t(r_1, r_2) = \varphi_0(r_1) r_2^{-1} f_t(r_2), \tag{5-74}$$

where $f_t(r_2)$ is the Massey-Moiseiwitsch trial function given in equation (2-15), the results given in Table 2-1 would be obtained. These results are an approximation to the exact phase shift for scattering by the static potential U alone. To include exchange effects, Massey and Moiseiwitsch (1951) use the function

$$\Psi_t^S(r_1, r_2) = [1 + (-1)^S P_{12}] \varphi_0(r_1) r_2^{-1} f_t(r_2), \tag{5-75}$$

where f_t again has the form (2-15) and in this case the results are approximations to the static exchange phase shifts. The most elaborate investigation of this kind has been carried out by Schwartz (1961) for s-wave and later extended by Armstead (1968) to p-waves. The trial wave functions were constructed using the fact, exploited in Rayleigh-Ritz calculations on the bound states of the two electron system by Hylleraas, that a trial function of the form $f(r_1, r_2, r_{12})$ where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ is an eigenfunction of total orbital angular momentum, belonging to the eigenvalue zero. A general form of the s-wave function is then

$$\Psi_t^S(\mathbf{r}_1, \mathbf{r}_2) = [1 + (-1)^S P_{12}]\left\{\varphi_0(r_2)r_1^{-1}\left[\sin kr_1 + \right.\right.$$
$$+ \tan \delta_0^S \left(1 - e^{-\lambda r_1/2}\right) \cos kr_1\right] \sum_{\ell mn} C_{\ell mn} e^{-\lambda/2(r_1 + r_2)} r_{12}^\ell r_1^m r_2^n \right\}.$$

$$\tag{5-76}$$

The first term in curly brackets has the correct asymptotic form
for large r_1, so that the remainder of the wave function van-
ishes at infinity and the exponential factors in the second term
provide the necessary cut-off for large r_1 or r_2. It is expected
that the expansion in powers of r_1, r_2 and r_{12} will be capable
of representing any kind of behaviour of the complete wave
function. The parameters $C_{\ell,m,n}$ and $\tan \delta_0^S$ can be found by
the Kohn procedure. Schwartz included as many terms in the
trial function as was necessary to secure convergence, using
up to 50 parameters. Because of the exponential cut-off, the
$1/r_1^2$ behaviour of the wave function for large r_1 is not easily
represented in this way and convergence is greatly improved
when additional terms having this property are added.

The phases obtained, which are included in Tables 5-2
and 5-3, represent the exact phases accurately. This conclu-
sion is supported by the results of the non-adiabatic method of
Temkin described in (5-5) below, and the method of variational
bounds developed by Gailitis (1965a,b).

The close coupling method

The complete wave functions can be exactly represented
by an expansion into a complete set of hydrogen atom eigen-
functions. By taking a finite number of terms in the expansion,
the truncated sum

$$\Psi_t^S(\mathbf{r}_1,\mathbf{r}_2) = [1 + (-1)^S P_{12}] \sum_{n=0}^{N} \varphi_n(\mathbf{r}_1) F_n(\mathbf{r}_2),$$

can be used as a trial function in the variational integral (5-12).
On varying each of the unknown functions $F_n(\mathbf{r})$, in place of the
single equation (5-15), we find a set of coupled integro-
differential equations

$$\int \varphi_n^*(\mathbf{r}_1)(H - E)\Psi_t^S(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1 = 0. \tag{5-77}$$

The boundary conditions satisfied by the unknown functions F_n
are (5-7) for $n = 0$ and $F_n(\mathbf{r}_1) \to 0$ as $r_1 \to \infty$ for $n \neq 0$.

Dipole polarization effects arise from the p states of
the hydrogen atom retained in the expansion. About 66% of the
polarizability arises from the 2p state, but only 82% arises
from all discrete p states, leaving 18% from the continuum,

and this suggests that the results may converge rather
slowly as more states are included in the expansion.
However, as will be shown later, the phase shifts ob-
tained in this way satisfy a minimum principle.   Below the
first excitation threshold, if the 1s – 2s – 2p states of hydrogen
are included in the expansion (Burke and Schey, 1962;
McEachren and Fraser, 1963) the resulting phase shifts lie between
half and three-quarters of the way between those of the static
exchange method and the exact phase shifts. The inclusion of
the 3s and 3p states (Burke and Schey, 1962) only improves the
results slightly, illustrating the slow rate of convergence.

Despite the poor convergence rate, results of outstand-
ing importance have been obtained within the close coupling
method: A narrow resonance in the singlet s phase shift,
superimposed on a smooth background was first discovered in
the 1s – 2s state approximation (Smith et al., 1962) and later
confirmed in the 1s – 2s – 2p approximation (Burke and Schey,
1962) at an energy (9.61 ev) just below the excitation threshold
(10.2 ev). The width of the resonance was about 0.11 ev. A
further resonance occurs in the 1s – 2s – 2p approximation in
the triplet p wave at 9.78 ev with a width ~ 0.009 ev, and
possibly there are also resonances in the singlet p and triplet
d waves. These resonances will be discussed in Chapter 7.
The close coupling method is also well adapted for use above
the first inelastic threshold, when the channels   in which the
electron moves relatively to the 2s and 2p states of hydrogen
are open, and this circumstance is, as we shall see, connected
with the success of the method in the description of resonances.

In a recent paper Damburg and Karule (1967) have shown
how the close coupling approximation can be modified so that
the long range dipole and the quadrupole polarizations are in-
cluded exactly and in which the extremal properties of the phase
are preserved. A transformation is made to a system in which
the axis of quantization is taken along the momentum of the
scattered electron (c.f. the helicity representation of Jacob and
Wick, 1959) and the expansion is in terms of perturbed eigen-
functions of the target. No applications have been reported as
yet.

Mixed trial functions

A more general trial function is obtained if a trial func-
tion of algebraic type is added to the truncated eigenfunction

expansion. Writing the trial function as

$$\Psi_t^S(\mathbf{r}_1,\mathbf{r}_2) = [1 + (-1)^S P_{12}]\left\{\sum_{n=0}^{N}\varphi_n(\mathbf{r}_1)F_n(\mathbf{r}_2) + \sum_{i=1}^{M}C_i\varphi_i(\mathbf{r}_1,\mathbf{r}_2)\right\},$$

$$(5-78)$$

where C_i are the variational parameters. The Kohn variation principle leads to the set of mixed integro-differential and algebraic equations (Gailitis, 1965a,b; Burke and Taylor, 1966)

$$\int\varphi_n^*(\mathbf{r}_1)(H - E)\Psi_t^S(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1 = 0, \quad n = 0, 1, 2, \ldots, N$$

$$(5-79)$$

$$\int\varphi_i(\mathbf{r}_1,\mathbf{r}_2)(H - E)\Psi_t^S(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2 = 0, \quad i = 1, \ldots, M.$$

As we shall see this method retains the minimum property of the phase shifts and the results necessarily improve as further algebraic terms or close coupling terms are added. If algebraic terms similar in form to those used by Schwartz (the second term in curly brackets in (5-76) are added to the 1s - 2s - 2p close coupling wave function, convergence is reached using about sixteen parameters and agreement with exact results is obtained.

5-5   THE NON-ADIABATIC SOLUTION OF TEMKIN

An alternative to the variational method that allows the calculation of phase shifts for $\ell = 0$ for the elastic scattering of electrons by hydrogen to arbitrary accuracy, has been introduced by Temkin (1962). If the total orbital angular momentum of the electron-hydrogen atom system is zero, the wave function is a function of r_1, r_2, and θ only, where $\cos\theta = \mathbf{r}_1 \cdot \mathbf{r}_2/r_1 r_2$, and can be expanded in the Legendre polynomial series,

$$\Psi^S(r_1,r_2,\theta) = r_1^{-1}r_2^{-1}\sum_{\ell=0}^{\infty}(2\ell + 1)^{1/2}\varphi_\ell^S(r_1,r_2)P_\ell(\cos\theta).$$

$$(5-80)$$

If this expression is inserted in the Schrödinger equation, a set of coupled equations for the functions φ_ℓ^S is obtained. The boundary conditions are

$$\varphi_\ell^S(r_1,0) = 0; \quad \varphi_0^S(r_1,r_2) \underset{r_1 \to \infty}{\sim} r_2\varphi_0(r_2)\sin(kr_1 + \delta_0^S),$$

$$(5\text{-}81)$$

and

$$\varphi_\ell^S(r_1,r_2) \sim 0 \quad \text{as} \quad r_1 \to \infty, \quad \ell \neq 0.$$

To ensure the correct symmetry of the wave function, we must have that

$$\varphi_\ell^S(r_1,r_2) = (-1)^S\varphi_\ell^S(r_2,r_1). \tag{5-82}$$

Because of this symmetry condition a solution is required only for $r_2 > r_1$ provided that the additional boundary conditions

$$\varphi_\ell^1(r_1, r_1) = 0, \left.\frac{\partial\varphi_\ell^0(r_2,r_1)}{\partial n}\right|_{r_1=r_2} = 0 \tag{5-83}$$

are satisfied, where the differentiation, $\partial/\partial n$, is carried out in a direction in the r_1, r_2 plane perpendicular to the line $r_1 = r_2$. Temkin has discussed various perturbative and non-perturbative methods for solving the truncated set of partial differential equations. In the lowest approximation, in which all the φ_ℓ are set equal to zero except for φ_0, φ_0 satisfies

$$\left(\frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2} + \frac{2}{r_2} + 2E\right)\varphi_0(r_1,r_2) = 0, \tag{5-84}$$

and this equation may be solved numerically. The solution is equivalent to that given by the close coupling equations in the approximation in which all s-states of the hydrogen atom are retained (both discrete and continuous). From the previous discussion of polarization, it is clear that to allow for dipole and quadrupole polarization the coupled equations for φ_0, φ_1 and φ_2 must be solved, in a sufficient approximation. The results of this calculational programme (Temkin, 1962; Temkin and Sullivan, 1963) agree very well with those of Schwartz and Gailitis. For example, the scattering lengths computed by

Temkin and Sullivan are $a_0^0 = -5.6$, $a_0^1 = -1.767$ and

those given by Schwartz are $a_0^0 = -5.965$, $a_0^1 = -1.769$.

The resonances discovered below the first excitation

threshold in the close coupling approximations can also be found by the non-adiabatic method and an additional singlet resonance is found in this way (Temkin, 1964). The formalism may be generalized for total angular momentum L greater than zero (Temkin and Bhatia, 1964), but unlike the other methods we have discussed, extension to systems of more than two electrons is hardly practicable, the importance of the work lying in the establishment of effectively exact results in the electron-hydrogen atom problem.

5-6   THE ESTABLISHMENT OF BOUNDS AND THE OPTICAL POTENTIAL

In Chapter 2, the Kohn variational method was shown to provide a lower bound to the scattering length in the case of potential scattering, provided that the trial function was of the form

$$\Psi_t = \Psi + \sum_{i=1}^{N} \lambda_i \varphi_i, \qquad (5\text{-}85)$$

where, if there are N bound states, the φ_i are approximate bound state eigenfunctions and the λ_i are parameters. The analysis can be generalized to many particle systems (Spruch and Rosenberg, 1960; Rosenberg et al., 1960) but it is necessary that the trial function should have the correct asymptotic form (for $\ell = 0$)

$$\Psi_t(\mathbf{r},\mathbf{x}) = \varphi_0(\mathbf{x})\left[A_t + \frac{1}{r}\right], \qquad (5\text{-}86)$$

where φ_0 is the target wave function. Unless the target wave function is known exactly, the scattering length obtained by the variational method will not obey a strict bound. It follows that strict bounds can only be obtained for collisions in which the target is a hydrogen atom, although in practice, if the target wave function is known to a good approximation, quite accurate variational calculations can be made.

In the triplet state no bound state of the electron-hydrogen atom system exists, and the Kohn variational method for electron-hydrogen atom scattering immediately provides a lower bound on the scattering length, but in the singlet state a single state of the negative hydrogen H^- exists with

$\epsilon = -0.75$ ev and the trial function must contain a term describing this state. When comparing different trial functions the one giving the largest value of the scattering length is the best, and the results (quoted in Table 5-2) of the variational calculations of Schwartz represent the best lower bounds on the scattering length at present.[6]

Projection operators and the optical potential

Above the threshold, it is possible to place a lower bound on the phase shift.[7] To do this we shall first describe a projection operator formalism due to Feshbach (1958, 1962), by which the scattering is described by an equivalent or 'optical' non-local potential. The method can be generalized to deal with systems with several open channels, but we shall continue to confine our attention at this point to energies below the first excitation threshold.

A projection operator $\mathbf{P}$ is introduced that projects the component of the wave function containing the open channel out of the complete wave function. For the scattering of electrons by hydrogen atoms, $\mathbf{P}$ is defined by the properties

$$\mathbf{P}\,\Psi^S(\mathbf{r_1},\mathbf{r_2}) \xrightarrow[r_1 \to \infty]{} \mathfrak{F}^S(\mathbf{r_1})\varphi_0(\mathbf{r_2}), \qquad (5\text{-}87a)$$

$$\xrightarrow[r_2 \to \infty]{} (-1)^S \mathfrak{F}^S(\mathbf{r_2})\varphi_0(\mathbf{r_1}), \qquad (5\text{-}87b)$$

where $\mathfrak{F}^S$ is given by (5-7).

It is clear that $\mathbf{P}$ defined in this way is highly non-unique, because it amounts to projecting <u>any</u> subspace containing the open channel out of the total Hilbert space for the problem. A particular choice is obtained by defining

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[6] Methods providing upper bounds can be formulated (Hahn, 1965; Sugar and Blankenbecler, 1964), but they are difficult to use in practice as the calculations of matrix elements of H^2 are usually involved.

[7] The results to be described here and in Chapter 6 are mainly due to Spruch and his collaborators (Hahn et al., 1962, 1963, 1964a,b). Equivalent results have been obtained by Sugar and Blankenbecler (1964) in the determinantal formalism. The work of Gailitis (1965a, b) and Rosenberg (1965) should also be consulted.

$$P = P_1 + P_2 - P_1 P_2, \tag{5-88}$$

where

$$P_1 \Psi^S (\mathbf{r}_1, \mathbf{r}_2) = \varphi_0(\mathbf{r}_1) \int_0^\infty \varphi_0^*(r_1') \Psi^S(\mathbf{r}_1', \mathbf{r}_2) d\mathbf{r}_1', \tag{5-89a}$$

$$P_2 \Psi^S (\mathbf{r}_1, \mathbf{r}_2) = \varphi_0(\mathbf{r}_2) \int_0^\infty \varphi_0^*(r_2') \Psi^S(\mathbf{r}_1, \mathbf{r}_2') d\mathbf{r}_2'. \tag{5-89b}$$

In this equation φ_0 is, as usual, the normalized ground state wave function of hydrogen. $(P_1 \Psi^S)$ has the asymptotic form of (5-87b) for large r_2, and vanishes for large r_1, while $(P_2 \Psi^S)$ satisfies condition (5-87a) for large r_1, and vanishes for large r_2. It is necessary to include the term $P_1 P_2$ in the definition (5-88) so that P satisfies $P^2 = P$, since although $P_1^2 = P_1$ and $P_2^2 = P_2$, $P_1 P_2$ is not zero. Using the completion expansion (5-43), the action of P is to project out a term of the same form as the first term in the series representing direct and exchange scattering.

$$P\Psi(\mathbf{r}_1, \mathbf{r}_2) = \varphi_0(\mathbf{r}_2)\overline{F}_0(\mathbf{r}_1) + \varphi_0(\mathbf{r}_1)\overline{G}_0(\mathbf{r}_2), \tag{5-90}$$

or if the symmetrized expansion,

$$\Psi^S(\mathbf{r}_1, \mathbf{r}_2) = \sum_{n=0}^\infty \left[\varphi_n(\mathbf{r}_2)F_n^S(\mathbf{r}_1) + (-1)^S \varphi_n(\mathbf{r}_1)F_n^S(\mathbf{r}_2) \right], \tag{5-91a}$$

is used, a term of the same form as the first term is again projected out

$$P\Psi^S = \varphi_0(\mathbf{r}_2)\overline{F}_0^S(\mathbf{r}_1) + (-1)^S \varphi_0(\mathbf{r}_1)\overline{F}_0^S(\mathbf{r}_2). \tag{5-91b}$$

The complexity of the projection operator arises from the identity of the target and scattered electrons, which ensures that the rearranged channel is always open. For positron-hydrogen atom scattering, at energies below the threshold for positronium formation, the boundary conditions on the wave functions are just those of equations (5-32, 5-33 and 5-34), where $\mathbf{r}_1$ is the coordinate of the positron, and a satisfactory projection operator would be given by P_1 of equation (5-89b).

If Q is defined by

$$Q = 1 - P, \tag{5-92}$$

Q, is the operator that projects out the part of the wave functions not included in $P\Psi$. We have that

$$Q^2 = Q, \quad QP = PQ = 0 \tag{5-93}$$

and

$$\Psi = (P + Q)\Psi. \tag{5-94}$$

By operating from the left on the Schrödinger equation, first with P and then with Q, the coupled equations

$$P(H - E)P\Psi = -PHQ\Psi, \tag{5-95a}$$

$$Q(H - E)Q\Psi = -QHP\Psi, \tag{5-95b}$$

are found, which are rigorously equivalent to the original Schrödinger equation. Equation (5-95b) can be solved formally, since

$$Q\Psi = \frac{-1}{Q(H - E)Q} QHP\Psi, \tag{5-96}$$

where no problems arise in the specification of the Green's function, since the continuum spectrum of the operator QHQ starts at the first excitation threshold. The wave function $Q\Psi$ represents some or all of the closed channels, so that

$$Q\Psi \to 0 \quad \text{as} \quad |r_1| \to \infty \quad \text{or} \quad |r_2| \to 0. \tag{5-97}$$

Substituting $Q\Psi$ into the equation for $P\Psi$, we find

$$[PHP + V_p - E]P\Psi = 0, \tag{5-98}$$

where V_p is the optical potential:

$$V_p = -PHQ \frac{1}{Q(H - E)Q} QHP. \tag{5-99}$$

To investigate the form of V_p, the Green's function $[Q(H - E)Q]^{-1}$ can be constructed from the eigenfunctions of QHQ, denoted by Φ_n, where

$$[QHQ - \epsilon_n]\Phi_n(r_1, r_2) = 0. \tag{5-100}$$

The Φ_n span the closed channel subspace, so that the normalization and closure conditions are

$$\langle \Phi_n, \Phi_m \rangle = \delta_{nm}; \quad \sum_n |\Phi_n\rangle\langle\Phi_n| = Q, \tag{5-101}$$

while $Q\Phi_n = \Phi_n;$ $P\Phi_n = 0.$ The optical potential is then

$$V_p = -\sum_n P H | \Phi_n \rangle \frac{1}{(\epsilon_n - E)} \langle \Phi_n | H P. \qquad (5\text{-}102)$$

Below the continuous spectrum of QHQ, which starts at the first excitation threshold, there may be a discrete spectrum at the energies $E = \epsilon_0^Q, \epsilon_1^Q, \epsilon_2^Q, \ldots$, but below this discrete spectrum, that is, for $E < \epsilon_0^Q$, V_p is a negative definite operator and represents an effective attraction. From the arguments given in Chapters 1 and 2, it follows that a phase shift computed from equation (5-98) with V_p set equal to zero must be less than the true phase shift. When P is given by (5-88, 5-89) and $V_p = 0$, we obtain the static-exchange approximation, which therefore provides a lower bound to the phase shifts. Further, if V_p is approximated by taking a finite number of terms in the sum in (5-102), then as the number of terms is increased so that the set of functions Φ_n spans more and more of the closed sub-space, the phase shift will steadily increase. This argument will hold, not only for the set of functions Φ_n, but for any set of functions spanning the Q space or part of the Q space.

If $Q\Psi$ is expanded in terms of a symmetrized set of hydrogen atom eigenfunctions, the phase shift for a given ℓ will increase steadily as the number of terms in the set increases, and at each stage of the calculation a lower bound is obtained. This expansion is identical with the close coupling expansion, which therefore always provides a bound on the phase shift. The same is true for the solution of the variational equation with the mixed algebraic and close coupling trial function referred to earlier (Gailitis, 1965a,b). The Kohn variational procedure will provide a bound even if the trial function for $Q\Psi$ is not orthogonal to $P\Psi$, as required by the relation $PQ = 0$. This is because (Burke and Taylor, 1966) any part of a trial function for $Q\Psi$ which is orthogonal to $P\Psi$ can be added to $P\Psi$ without altering the asymptotic form of $P\Psi$.

The discrete eigenvalue spectrum of QHQ gives rise to singularities in the optical potential, which, as we shall see, lead to resonances in elastic scattering of the kind discussed in Chapter 4. Following similar arguments to those given in Chapter 2, it can be shown that for all energies below the continuum of QHQ the lower bound on the phase shift is

retained, provided the trial function contains the same number of discrete states of **QHQ** as the exact wave function. Care has to be taken under these circumstances to define the phase shift in a consistent manner. For example, when $\mathbf{Q}\Psi_t$ is set equal to zero, the phase shift is determined by applying the modified Levinson's theorem to the static-exchange equation. If $\mathbf{Q}\Psi_t$ is gradually extended, then the phase shift will increase until, when sufficient of the Q-space is spanned by $\mathbf{Q}\Psi_t$, a resonance will appear at the first excitation energy of the system. As $\mathbf{Q}\Psi_t$ is further improved the resonance will move to lower energies and when it reaches a particular energy, the phase shift at that energy will increase by π. If there are N resonances below the energy under consideration, and if in the absence of V_p the phase shift satisfies $0 < \delta < \pi$, then the true phase shift will satisfy $N\pi < \delta < (N + 1)\pi$.

Another way of using the bound property is to construct inequalities of the kind (such as (2.32b)) that we discussed in connection with bounds on the scattering length. If the wave function is expanded in eigenfunctions of angular momentum, denoted by Ψ^ℓ, then $\mathbf{P}\Psi^\ell$ can be defined by

$$\mathbf{P}\Psi^\ell \xrightarrow[r_1 \to \infty]{} \varphi_0(r_2) r_1^{-1}\left[\cos\left(kr_1 - \frac{\ell\pi}{2}\right) + \tan\delta_\ell \sin\left(kr_1 - \frac{\ell\pi}{2}\right)\right] P_\ell(\cos\theta_1)$$

At energies below the discrete spectrum of **QHQ** the following inequality can be shown to hold (Hahn, 1965)

$$\tan\delta_\ell \geq \tan\delta_\ell^A - (2\pi k)^{-1}\left(\mathbf{Q}\Psi_t^\ell, (H - E)\Psi_t^\ell\right), \qquad (5\text{-}103)$$

where δ_ℓ^A is the phase shift computed from the equation

$$\mathbf{P}(H - E)\mathbf{P}\Psi^\ell = -\mathbf{P}H\mathbf{Q}\Psi^\ell. \qquad (5\text{-}104)$$

The polarized orbital method   and bounds

The polarized orbital method can be modified in various ways so that it provides a variational bound. Consider as an example the case of positron scattering by hydrogen atoms. With the projection operator for the ℓth partial wave defined as

$$\mathbf{P}^\ell\Psi(\mathbf{r}_1,\mathbf{r}_2) = \varphi_0(r_1)P_\ell(\cos\theta_2)\int d\cos\theta_2'\int dr_1'\varphi_0^*(r_1')P_\ell(\cos\theta_2')\Psi(\mathbf{r}_1',\mathbf{r}_2')$$

$$= r_2^{-1}\varphi_0(r_1)F_\ell(r_2)P_\ell(\cos\theta_2), \qquad (5\text{-}105)$$

where $F_\ell(r)$ is a function with the asymptotic form:—

$$F_\ell(r) \sim \sin\left(kr - \frac{\ell\pi}{2}\right) + \tan \delta_\ell \cos\left(kr - \frac{\ell\pi}{2}\right),$$

the first of the coupled equations (5-95) becomes

$$(\nabla^2 - U^+(r) + k^2)F_\ell(r) = 2\int d\Omega_2' \int dr_1' \varphi_0^*(r_1')P_\ell(\cos \theta_2')HQ\Psi,$$

(5-106)

where U^+ is the static interaction between the positron and the hydrogen atom. This is repulsive, and is just equal and opposite to the corresponding interaction for electron–hydrogen atom scattering,

$$U^+ = 2\left(1 + \frac{1}{r}\right)e^{-2r}.$$

(5-107)

If **Q** is taken to be of the form

$$Q\Psi = \varphi_{pol}(r_1, r_2)r_2^{-1}F_\ell(r_2)P_\ell(\cos \theta_2),$$

(5-108)

where φ_{pol} is the distorted wave function of the hydrogen atom in the adiabatic approximation, equation (5-106) reduces to that of the polarized orbital method

$$\left(\nabla^2 - U^+(r) - U_p(r) + k^2\right)F_\ell(r) = 0,$$

(5-109)

where U_p is the second order polarization potential. The effect of polarization in this case is much greater than for the electron–hydrogen atom case. The potentials U^+ and U_p are now of opposite sign, but at low energies the net effect is attractive.[8] The solution of equation (5-109) does not provide a bound on the phase shifts, but a bound is given by using the solutions in equation (5-103). The second term on the right hand side of (5-103) corrects to some extent for the adiabatic

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[8] Positron-atom scattering in the polarized orbital approximation has been discussed by Cody et al. (1964), Bransden and Jundi (1966), Kester et al. (1965), Callaway et al., (1968), Drachman (1965, 1968). A general review of positron scattering, with a full bibliography, has been given by Bransden (1969).

approximation.

Similar extensions of the polarized orbital method can be obtained by using as a trial function in the Kohn method Ψ_t, where

$$\Psi_t(\mathbf{r}_1,\mathbf{r}_2) = \left[\varphi_0(\mathbf{r}_1) + \varphi_{pol}(\mathbf{r}_1,\mathbf{r}_2)\right] F(\mathbf{r}_2), \qquad (5\text{-}110)$$

or, equivalently, using the projection operator

$$\mathbf{P} = \left[\varphi_0(\mathbf{r}_1) + \varphi_{pol}(\mathbf{r}_1,\mathbf{r}_2)\right] \int d\mathbf{r}_1' \int d\mathbf{r}_2' \left[\varphi_0(\mathbf{r}_1') + \varphi_{pol}(\mathbf{r}_1',\mathbf{r}_2')\right].$$

$$(5\text{-}111)$$

This has been examined by Callaway et al. (1968), who found the resulting equivalent potential, which is known as the extended polarization potential.

In order to satisfy the condition $\mathbf{P}^2 = 1$, the perturbed wave function

$$\left[\varphi_0(\mathbf{r}_1) + \varphi_{pol}(\mathbf{r}_1,\mathbf{r}_2)\right]$$

must be normalized to unity for all $\mathbf{r}_2$. Using this condition,[9] the final form of the wave equation for $F(\mathbf{r}_2)$ is (for $e^+ - H$ scattering)

$$\left[\nabla_2^2 - U^+(\mathbf{r}_2) - U_p(\mathbf{r}_2) - U_D(\mathbf{r}_2) + k^2\right] F(\mathbf{r}_2) = 0, \quad (5\text{-}112)$$

where U^+ and U_p are the usual static and polarization potentials and U_D, the distortion potential, is

$$U_D(\mathbf{r}_2) = \int |\nabla_{\mathbf{r}_2}\varphi_{pol}(\mathbf{r}_1,\mathbf{r}_2)|^2 d\mathbf{r}_1. \qquad (5\text{-}113)$$

For electron scattering exchange terms must be added to equation (5-112), and there is apparently some difficulty in finding a correct projection operator and the resulting phase shifts may not provide a bound. The adiabatic polarization potential predicts phase shifts for positron–hydrogen atom scattering that are more attractive than those given by the elaborate variational calculations of Schwartz and the effect of the corrections

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[9] This condition is satisfied when φ_{pol} is obtained from perturbation theory.

provided by the extended polarization method is to diminish the attraction considerably, but we shall not enter into the details here.

5-7   ELASTIC SCATTERING OF ELECTRONS BY COMPLEX ATOMS

Helium

The general method outlined in the earlier parts of this chapter can be applied to the scattering of electrons by complex atoms, if the target wave functions are given in some approximation. With some exceptions most calculations have been based on Hartree or Hartree-Fock wave functions,[10] which are of the form of products of one particle wave functions. In the most simple example, the ground state of helium, which is a singlet state of zero orbital angular momentum, the Hartree-Fock wave function is

$$\varphi_0(\mathbf{r}_1, \mathbf{r}_2)\chi_{s=0}(1,2) = \left[\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2) + \varphi_b(\mathbf{r}_1)\varphi_a(\mathbf{r}_2)\right] \times$$

$$\times \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)], \qquad (5\text{-}114)$$

and the functions $\varphi_{a,b}$ are determined by taking $\varphi_0(\mathbf{r}_1, \mathbf{r}_2)$ as a trial function in the variational method. This leads to nonlinear equations for $\varphi_{a,b}$ which are solved by an iterative method: the self-consistent field method. In applications the one electron functions can often be represented quite accurately by analytic forms. In the case of helium, the simple choice

$$\varphi_a(r_1) = N_a \exp(-\lambda_a r_1); \quad \varphi_b(r_1) = N_b \exp(-\lambda_b r_2)$$

is quite effective.

For two and three electron atoms it is feasible to employ parametric wave functions of the Hylleraas type and for the helium ground state it is often sufficient to use the very simple

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[10]For a general account of atomic structure see Slater (1960).

approximation

$$\varphi_0(r_1, r_2) = Ne^{-\lambda(r_1 + r_2)}, \tag{5-115}$$

where λ is determined by the variational (Rayleigh-Ritz) method to be (atomic units)

$$\lambda = 1.6875, \tag{5-116}$$

and represents the effective charge seen by one electron moving in the Coulomb field of the nucleus screened by the second electron.

The static exchange approximation for elastic scattering is based on the trial function

$$\Psi(r_1, r_2, r_3) = \left[1 - P_{23} + P_{13}\right] \times$$
$$\times \left[\varphi_0(r_2, r_3) F_0(r_1) \chi_{\frac{1}{2}, \pm\frac{1}{2}}(1, 2, 3),\right] \tag{5-117}$$

where P_{ij} is an operator that exchanges all the coordinates (including spin) of particles i and j and $\chi_{s,m}(1, 2, 3)$ is the doublet spin function

$$\chi_{\frac{1}{2}, \pm\frac{1}{2}}(1, 2, 3) = \frac{1}{\sqrt{2}} \left.\begin{matrix} \alpha(1) \\ \beta(1) \end{matrix}\right\} \left[\alpha(2)\beta(3) - \beta(2)\alpha(3)\right]. \tag{5-118}$$

With this wave function an integro-differential equation for $F_0(r)$ is obtained which is similar to equation (5-16), for electron-hydrogen atom scattering. The radial equations have been solved by Morse and Allis (1933) for the partial waves $l = 0$ and $l = 1$, and for $l = 2$ (d-wave) by Massey et al. (1966). Morse and Allis found that if the exchange kernel was neglected it was impossible to obtain reasonable agreement with the measured cross section, particularly at the lowest energies. The results of the static exchange approximation agree rather well with the measured total cross sections and reasonably well with the differential cross sections (see Fig. 5-3).

To include the effects due to the distortion of the atom, the polarized orbital method of Temkin and Lamkin may be used. The polarized wave function is again written in the Hartree-Fock form (5-114), but the single electron functions $\varphi_{a,b}$ are modified by

$$\varphi_i(\mathbf{r}_i) \to \varphi_i(\mathbf{r}_i) + \varphi_i^p(\mathbf{r}_i, \mathbf{x}),$$

Table 5-4

Parameters in the long range part of the effective potential between an electron and an atom in the ground state

(see equation 5-64)

	H	He	Ne	A	Kr	Xe	Li	Na	K
				Atomic units					
α_1	4.5	1.39	2.67	11.1	16.8	27.1	160	160	270
α_2	15	2.41	9.0	72.9	--	--	--	--	--
β_1	5.375	0.706	1.27	8.33	14.50	29.15	1.18×10^3	1.1×10^3	2.4×10^3

where $\mathbf{x}$ is the position vector of the scattered electron. φ^p
may be calculated to first order in perturbation theory, if the
adiabatic approximation is used.

Several calculations have been performed in the adia-
batic exchange approximation, in which the polarization poten-
tial V_p is included, but the modification of the exchange
kernel (which is not expected to be important) is ignored
(Labahn and Callaway, 1964; Lawson et al., 1966). The
polarization potential is not as important as in the case of
hydrogen because of small polarizability of helium (see Table
5-4). The angular distributions calculated by Lawson et al.
(1966) are shown in Fig. 5-3, together with the experimental
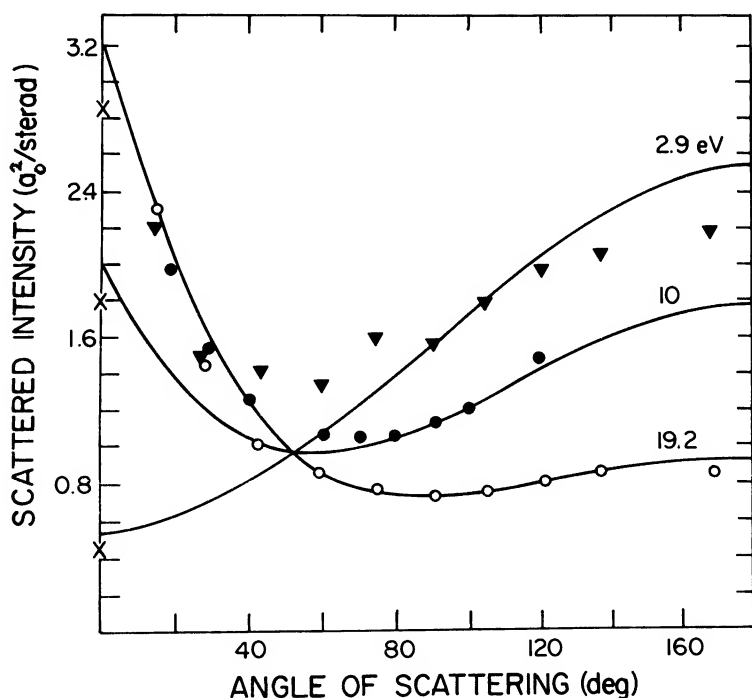
Figure 5-3.   Angular distributions for the elastic scattering of electrons by helium.
The full lines are the calculated values in the exchange-adiabatic approximation by
Lawson et al. (1966).   The experimental points are due to Ramsauer and Kollath (1932).

data. Agreement is good at 10 and 19.2 ev, but the approxima-
tion appears to be inadequate at the lowest energy of 2.5 ev.
Callaway et al. have used their extended polarization potential,
which compensates to some extent for adiabatic approximation,
to calculate the elastic scattering phase shifts for $\ell < 2$. In
this approximation the effect of polarization, which is over-
estimated in the adiabatic method, is reduced and rather good
agreement is obtained with the total cross section (Fig. 5-4).

Measurements have also been made of the momentum
transfer cross section, which is a measure of the average forward
momentum of the projectile lost in a collision. In the center of
mass system, the change in the forward momentum of the pro-
jectile is $\mu v(1 - \cos \theta)$ where μ is the reduced mass, v the
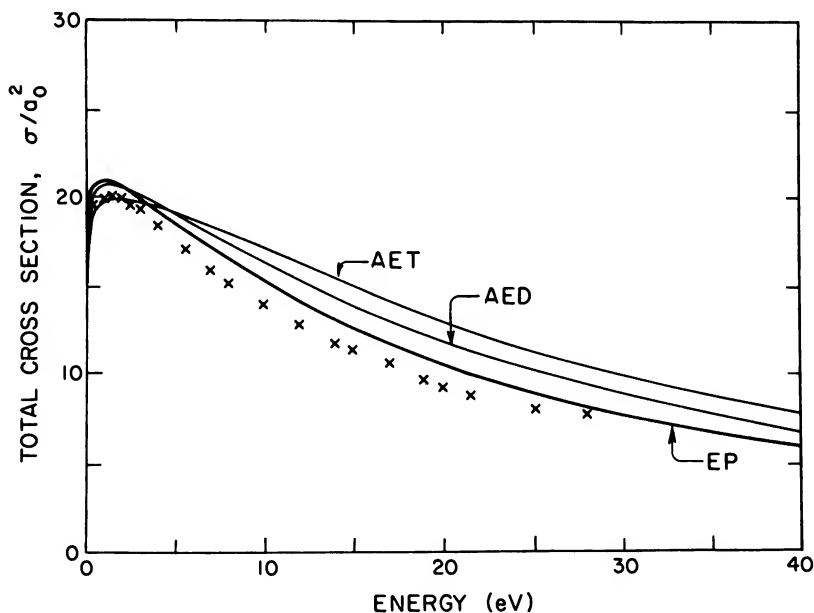
Figure 5-4.   The total elastic cross section for electron helium scattering.

    E.P.   Extended polarization potential.[a]
    AED   Adiabatic exchange potential with dipole component.[a]
    AET   Adiabatic exchange potential with (Monopole + dipole + quadrupole)
             components.[a]
    x   Experimental points of Golden and Bandel (1965).
    (a)   Callaway et al. (1968).

relative velocity and θ is the scattering angle. The momentum transfer cross section is then defined as

$$\sigma_D = \int (1 - \cos\,\theta)\left(\frac{d\sigma}{d\Omega}\right) d\Omega, \qquad (5\text{-}119)$$

where $(d\sigma/d\Omega)$ is the usual differential cross section. If the scattering is isotropic, it is clear that $\sigma_D = \sigma$, where σ is the total cross section; but if the scattering is concentrated in the forward direction $\sigma_D < \sigma$ while if it is concentrated in the backward direction $\sigma_D > \sigma$.

For electron-helium collisions the measurements of the momentum transfer cross section agree rather well with the predictions of the extended polarization method (Fig. 5-5).
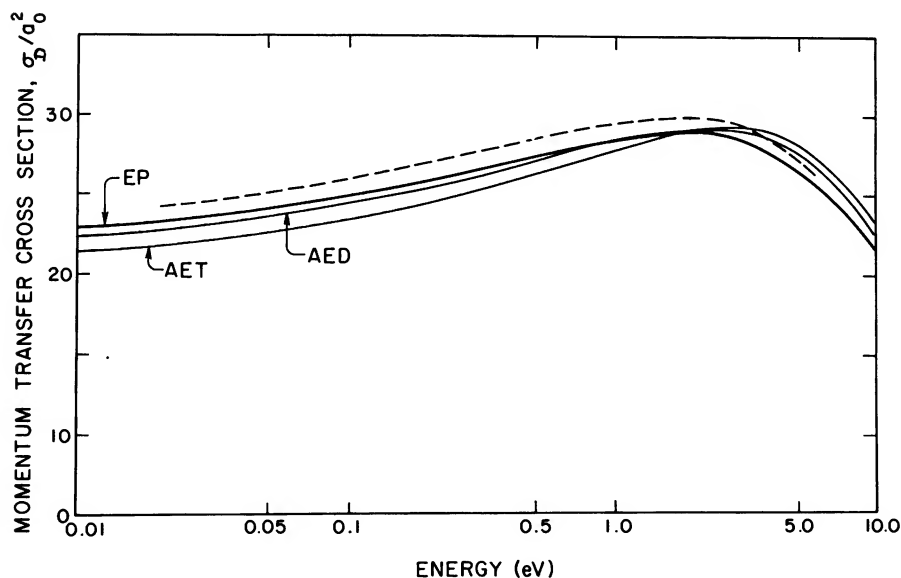
Figure 5-5.   The momentum transfer cross section for electron-helium scattering. EP, AED, AET — see caption to figure 5-3. Experimental curve from Crompton et al. (1967).

The inert gases

Using the Hartree-Fock wave functions for the target, polarized orbital calculations have been carried out for argon and neon (Thompson, 1966). The results for both the total and differential cross sections are remarkably good, the Ramsauer-Townsend minimum in the cross section being well reproduced in argon. Earlier calculations by Holtsmark (1930), using a semi-empirical polarization potential, include the case of electron-kryptron scattering for which good agreement is also obtained. The parameters of the long range part of the potential are shown in Table 5-4.

Oxygen

The ground state of the oxygen atom is in a $2p^4$ configuration, the 3P term lying lowest. The total spin of an electron-oxygen atom system is then either $S = 1/2$ or $S = 3/2$. Bates and Massey (1943, 1947) calculated the s-wave phase shifts for each spin state using an empirical polarization term and, more recently, polarized orbital calculations have been made by Temkin (1957) and Henry (1967). In the work of Henry the dipole polarization terms were calculated assuming that no contribution arose from the closed $1s^2$ shell, that the 2s shell wave functions were perturbed only by p-states, and the 2p shell wave functions by s and d states. The calculated polarizability of 5.15 agrees well with that found experimentally (5.19). Using these results, the cross section for photo-detachment from the oxygen negative ion 0^- can be calculated and compares rather favourably with experiment.

It is probably safe to conclude that the polarized orbital method gives a good account of the elastic scattering by those atoms for which polarization is not large. It cannot reproduce the resonances, where these are observed, and does not work well for the alkali atoms where the polarizability is very high (Karule, 1965).

The alkali atoms

In the ground state of the alkali atoms there is a single valence electron in an s-state outside closed inner shells. The polarizability is large (see Table 5-4) and the coupling between the ground state and first excited p state contributes at least 98% of the sum (5-35) that determines $U_p(r)$. It follows that a good approximation is the inclusion of just these states, the s- and

p-states, in the close coupling expansion. This has been done by Karule (1965) for energies below the excitation threshold[10] (5 ev) for Li, Na, K and Cs. Up to eight partial waves were included, and for $\ell > 4$ exchange was not important and was ignored. The cross sections obtained above 2 ev are only about half those measured by Perel et al. (1962).

5-8   FORWARD DISPERSION RELATIONS

It can be shown for a large class of short range potentials that the forward scattering amplitude is analytic as a function of energy (Martin, 1965) with the exceptions of the cut along the real energy axis due to unitarity and of poles at the bound state energies. It is then possible to write a dispersion relation for the combination $[f(E, \theta = 0) - f_B(E, \theta = 0)]$, where f_B is the amplitude for the Born approximation, by applying Cauchy's theorem to a contour bordering the cut and closed by an infinite circle in the E-plane. We find that

$$\text{Re}\{f(E,0) - f_B(E,0)\} = [\text{Pole terms}] + \frac{1}{\pi} P \int_0^\infty \frac{\text{Im}[f(E',0)]}{(E' - E)} dE'.$$

$$(5-120)$$

Assuming that such a dispersion relation applies to electron scattering by atoms, Lawson et al. (1966) have analyzed the cross section for electron-helium scattering. In this case, as no bound states of He⁻ exist, there are no pole terms and the Born approximation amplitude is given by

$$f_B(E,0) = -\frac{1}{2\pi} \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \left\{ [\varphi_0(\mathbf{r}_1, \mathbf{r}_2)]^2 \left[-\frac{2}{r_3} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_3|} + \right. \right.$$

$$\left. + \frac{1}{|\mathbf{r}_2 - \mathbf{r}_3|} \right] - \varphi_0(\mathbf{r}_1, \mathbf{r}_2) \varphi_0(\mathbf{r}_3, \mathbf{r}_2) e^{i\mathbf{k} \cdot (\mathbf{r}_3 - \mathbf{r}_1)} \left[-\frac{2}{r_3} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_3|} + \right.$$

$$\left. \left. + \frac{1}{|\mathbf{r}_2 - \mathbf{r}_3|} \right] \right\},$$

$$(5-121)$$

---

where the electrons are labelled 1, 2 and 3; φ_0 is the ground state wave function of helium, and the second term in curly brackets is due to electron exchange.

By the optical theorem, $\text{Im}[f(E,0)]$ (which occurs under the integral in (5-120)) can be related to the total cross section by

$$\text{Im}[f(E,0)] = \frac{k}{4\pi}\,\sigma_{tot}(E).\qquad\qquad(5\text{-}122)$$

Using the observed total cross sections at low energies and the Born approximation cross section at high energies, Lawson et al. calculated $\text{Re}[f(E,0)]$ from the dispersion relation. These results were then compared with the results of theoretical calculations using the polarized orbital method and rather satisfactory agreement was found. Some results are illustrated in Fig. 6-4 of the next chapter. An experimental test is not directly possible, as differential cross sections are not known experimentally in the forward direction; however, the dispersion relation points at $\theta = 0$ appear to extrapolate smoothly from the angular region ($>15° - 20°$) where measurements exist. In the low energy region, from 2 to 20 ev, the forward scattered intensities, calculated from the dispersion relation, are shown as crosses in Fig. 5-3.

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Chapter 6

SCATTERING OF ELECTRONS BY ATOMS
ABOVE THE INELASTIC THRESHOLD

In the last chapter, the scattering of electrons below
the first excitation threshold was discussed. In this energy
interval the scattering is purely elastic, although, because of
the identity of the scattered and target electrons, exchange
scattering, which can be considered as a particular case of a
rearrangement collision, is always possible. Above the in-
elastic threshold the elastic scattering can still be treated as
a potential problem, but the effective (optical) potential V_p
becomes complex, to allow for the loss of probability flux
from the initial state. Using the optical theorem, such a treat-
ment allows a calculation of the total cross section, but not of
the cross sections for individual inelastic processes. To cal-
culate individual cross sections most of the methods discussed
for elastic scattering can be applied, provided the trial function
contains components referring to both the incident and final
channels and, in addition, methods based on perturbation
theory are of considerable importance.

6-1 THE CLOSE COUPLING APPROXIMATION AND BOUNDS ON THE REACTION MATRIX

The exact wave function can be expanded in a complete
set of target eigenfunctions under all circumstances, and above
an inelastic threshold it is reasonable to use a truncated ex-
pansion as a trial function in the variational expression as

before. If the integral I is defined as

$$I = \int \Psi^*(H - E)\Psi d\tau \qquad\qquad (6\text{-}1)$$

then $\delta I = 0$, under arbitrary variaiions in Ψ, provided that the trial functions satisfy boundary conditions of the same form as the exact functions. If $\delta I = 0$, the error in the scattering amplitude, or the reaction matrix, depending on the normalization adopted, will be of the second order. It follows that the coupled equations for the functions $F_n(\mathbf{r})$ are the same as those obtained for elastic scattering (5-77), but the boundary conditions satisfied by such of the F_n that represent open channels are now those specified in Chapter 4, equation (4-70). In the basis in which the angular momentum is diagonal, the equations are of the form (4-75) and the boundary conditions are those of equations (4-76). If the trial function Ψ is properly symmetrized, thus allowing for exchange, the potentials $V_{\gamma\gamma'}$ are integral operators rather than simple local interactions. It is of course possible to add to the truncated eigenfunction expansion algebraic terms and to construct a trial function of the form (5-78), and in applications correlation effects can be allowed for in this way.

For elastic scattering, we saw that in many cases reasonably accurate results can be obtained (for example in electron-hydrogen atom scattering) in the static exchange approximation, which is the lowest order close coupling approximation. This is because the energy gap between the ground and excited states of an atom is comparatively large and the coupling correspondingly weak. For a reaction in which the ground state of an atom is excited, at least the ground state and the particular excited state of interest must occur in the expansion of the wave function and the energy of the excited state may be very close to that of many other states, and these states will be coupled strongly to the system. Under these circumstances the convergence of the method may be poor. Burke et al. (1967a) have suggested that the close coupling method should succeed if all the open channels are included in the expansion, except at energies immediately below the next highest threshold. An additional advantage of including all the open channels in the expansion is that the calculation then provides a bound on the elements of the reaction matrix. This is a

generalization of the result that the close coupling method provides a bound in the phase shift, in the case of a single open channel.

Bounds on the reaction matrix

In a single channel problem, it was shown that the phase shift was a monotonic function of the potential. The proof depended upon the potential being real and was only applicable to scattering that was purely elastic. When the potential is not local, but is an integral operator, the proof will still hold, if the potential operator is both self-adjoint and real. The extension of this result to many channel scattering has been discussed by several authors (Hahn et al., 1964a,b; Sugar and Blankenbecler, 1964) and we shall follow an argument due to Gallitis (1964).

Suppose that there are N open channels, then the channel wave functions $f_{\gamma,a}(r)$ satisfy coupled equations of the form

$$L_{\gamma} f_{\gamma,a}(r) = \sum_{\gamma'=1}^{N} V_{\gamma\gamma'} f_{\gamma',a}(r), \quad \begin{array}{l} \gamma = 1,2, \ldots N, \\ a = 1,2, \ldots N, \end{array} \quad (6\text{-}2a)$$

where

$$L_{\gamma} = \frac{\hbar^2}{2\mu_{\gamma}} \left(\frac{d^2}{dr^2} - \frac{\ell_{\gamma}(\ell_{\gamma}+1)}{r^2} + k_{\gamma}^{2} \right). \quad (6\text{-}2b)$$

The potential matrix $\mathbf{V}$ will be taken to be real and symmetrical and will be, in general, non-local so that

$$V_{\gamma\gamma'} f_{\gamma',a} \longrightarrow \int_{0}^{\infty} V_{\gamma\gamma'}(r,r') f_{\gamma',a}(r') dr'.$$

The effects of the closed channels can be described through the effective potential $\mathbf{V}$, just as we discussed in Chapter 5 for the case of scattering in which only a single channel was open. An expression for $\mathbf{V}$ is found below in equation (6-10). The channel wave functions can be defined to be real, with the boundary conditions (4-76):—

$$f_{\gamma,a}(0) = 0,$$

$$f_{\gamma,a}(r) \sim k_\gamma^{-1}\left[s_\ell(k_\gamma r)\delta_{\gamma a} + \sqrt{\left(\frac{\mu_\gamma k_\gamma}{\mu_a k_a}\right)}\,c_\ell(k_\gamma r)K_{\gamma a}\right], \quad (6-3)$$

where **K** is the reaction matrix. Let us also consider a second set of equations similar to equations (6-2), but in which the potential matrix **V** is replaced by a different potential matrix **V̄**, so that

$$L_\gamma \bar{f}_{\gamma,a}(r) = \sum_{\gamma'=1}^{N} \bar{V}_{\gamma\gamma'}\bar{f}_{\gamma',a}(r), \quad \begin{array}{l} \gamma = 1,2,\ \ldots\ N, \\ a = 1,2,\ \ldots\ N. \end{array} \quad (6-4)$$

By multiplying equations (6-2) by $\bar{f}_{\gamma,\beta}$ and equations (6-4) by $f_{\gamma,\beta}$, subtracting the two sets of equations and summing over γ, we find that

$$\sum_{\gamma=1}^{N} \left\{\bar{f}_{\gamma,\beta}(r)L_\gamma f_{\gamma,a}(r) - f_{\gamma,\beta}(r)L_\gamma \bar{f}_{\gamma,a}(r)\right\}$$

$$= \sum_{\gamma,\gamma'=1}^{N} \left\{\bar{f}_{\gamma,\beta}(r)V_{\gamma\gamma'}f_{\gamma',a}(r) - f_{\gamma,\beta}(r)\bar{V}_{\gamma\gamma'}\bar{f}_{\gamma',a}(r)\right\}.$$

We now add these equations to the equations formed by interchanging a and β. On integrating over r, we obtain

$$\sum_{\gamma=1}^{N}\left(\frac{\hbar^2}{2\mu\gamma}\right)\int_0^R dr\left[\bar{f}_{\gamma,\beta}(r)\frac{d^2}{dr^2}f_{\gamma,a}(r) - f_{\gamma,a}(r)\frac{d^2}{dr^2}\bar{f}_{\gamma,\beta}(r) + \right.$$

$$\left. + \bar{f}_{\gamma,a}(r)\frac{d^2}{dr^2}f_{\gamma,\beta}(r) - f_{\gamma,\beta}(r)\frac{d^2}{dr^2}\bar{f}_{\gamma,a}(r)\right]\ .$$

$$= \sum_{\gamma,\gamma'=1}^{N}\int_0^R dr\left[\bar{f}_{\gamma,\beta}(r)\left(V_{\gamma\gamma'} - \bar{V}_{\gamma\gamma'}\right)f_{\gamma',a}(r) + \right.$$

$$\left. + f_{\gamma,\beta}(r)\left(V_{\gamma\gamma'} - \bar{V}_{\gamma\gamma'}\right)\bar{f}_{\gamma',a}(r)\right], \quad (6-5)$$

where on the right hand side the symmetry of $\mathbf{V}$ and $\bar{\mathbf{V}}$ has been employed. On integrating by parts the left hand side of the equations reduces to

$$\sum_{\gamma=1}^{N} \left(\frac{\hbar^2}{2\mu_\gamma}\right)\left[\left(\bar{f}_{\gamma,\beta}(r)\frac{d}{dr}f_{\gamma,a}(r) - f_{\gamma,a}(r)\frac{d}{dr}\bar{f}_{\gamma,\beta}(r)\right) + \right.$$

$$\left. + \left(\bar{f}_{\gamma,a}(r)\frac{d}{dr}f_{\gamma,\beta}(r) - f_{\gamma,\beta}(r)\frac{d}{dr}\bar{f}_{\gamma,a}(r)\right)\right]_0^R .$$

On taking the limit $R \to \infty$ and using the asymptotic form of the functions $f_{\gamma,a}$ and $\bar{f}_{\gamma,a}$, given by equation (6-3), this expression reduces to (using the fact that K is symmetrical)

$$\left(\frac{\hbar^4}{\mu_a\mu_\beta k_a k_\beta}\right)^{\frac{1}{2}}\left(\bar{K}_{\beta a} - K_{\beta a}\right), \qquad (6-6)$$

and we can write finally, using a matrix notation, that

$$(\bar{\mathbf{K}} - \mathbf{K}) = \boldsymbol{\rho}\int_0^\infty \left(\bar{\mathbf{f}}^T(\mathbf{V}-\bar{\mathbf{V}})\mathbf{f} + \mathbf{f}^T(\mathbf{V}-\bar{\mathbf{V}})\bar{\mathbf{f}}\right)dr\,\boldsymbol{\rho}, \qquad (6-7)$$

where $\mathbf{f}^T$ denotes the transpose of the matrix $\mathbf{f}$ and $\boldsymbol{\rho}$ is a diagonal matrix

$$\rho_{a\beta} = \delta_{a\beta}\left(\frac{k_a\mu_a}{\hbar^2}\right)^{\frac{1}{2}}. \qquad (6-8)$$

It follows that if $\bar{\mathbf{V}} < \mathbf{V}$, then $\bar{\mathbf{K}} > \mathbf{K}$ provided the reaction matrix $\mathbf{K}$ varies continuously from $\mathbf{K}$ to $\bar{\mathbf{K}}$ as $\mathbf{V}$ varies from $\mathbf{V}$ to $\bar{\mathbf{V}}$. By the inequality $\bar{\mathbf{K}} > \mathbf{K}$, we mean that $(\bar{\mathbf{K}} - \mathbf{K})$ is a positive matrix, which requires that

$$\boldsymbol{\psi}^T(\bar{\mathbf{K}} - \mathbf{K})\boldsymbol{\psi} > 0, \qquad (6-9)$$

for all real column vectors Ψ. If a matrix is positive, it follows that the eigenvalues and the trace of the matrix are all positive, but individual elements of the matrix may not be. In particular (6-9) implies that the sum of the eigenphase shifts

for the potential $\bar{\mathbf{V}}$ will be greater than the sum for $\mathbf{V}$.

The continuity of $\mathbf{K}$ with the potential is essential to the argument, for if one of the eigenphases passes through $\pi/2$ as we pass from $\mathbf{V}$ to $\bar{\mathbf{V}}$, $\mathbf{K}$ will become infinite at that point. However, at such a point the inverse reaction matrix $\mathbf{K}^{-1}$ will be continuous and this implies that the S matrix is always continuous in $\mathbf{V}$. Writing $\bar{\mathbf{S}} = \mathbf{S} \exp(i\boldsymbol{\gamma})$ we have, if $\bar{\mathbf{V}} < \mathbf{V}$, that $\boldsymbol{\gamma}$ is always a positive matrix.

To use these results all that is necessary is to extend the definition of the projection operator $\mathbf{P}$ (page 214), so that it projects, from the complete space spanned by the target eigenfunctions any sub-space that includes all the open channels. The coupled equations for $\mathbf{P}\Psi$ and $\mathbf{Q}\Psi$ can again be written in the form

$$\mathbf{P}\,(H - E)\,\mathbf{P}\,\Psi = -\mathbf{P}\,H\mathbf{Q}\Psi,$$

$$\mathbf{Q}\,(H - E)\mathbf{Q}\Psi = -\mathbf{Q}H\mathbf{P}\,\Psi,$$

where the equation for $\mathbf{P}\Psi$ is now a matrix equation like (6-2). Provided all the open channels are included in $\mathbf{P}\Psi$, the matrix optical potential

$$\mathbf{V}_{\mathbf{p}} = -\mathbf{P}\,H\mathbf{Q}\,\frac{1}{\mathbf{Q}(H - E)\mathbf{Q}}\mathbf{Q}H\mathbf{P}, \qquad\qquad (6\text{-}10)$$

is a negative definite operator, below the eigenvalue spectrum of $\mathbf{Q}H\mathbf{Q}$, and it follows that as the space spanned by $\mathbf{Q}\Psi$ is progressively enlarged $\mathbf{V}_{\mathbf{P}}$ becomes more and more negative.

At each stage the eigenphases calculated from the solution of the coupled equations provide a lower bound. In particular, the close coupling equations provide a bound on the eigenphases which is improved as the closed channels are added, either directly or through algebraic trial functions.

Two state approximations

When it is not feasible to take into account all the open channels, the approximation in which the coupled equations of the eigenfunction expansion method are reduced to those connecting the incident channel and the excited state of interest, may be good if these two states are strongly coupled compared to the coupling with other states. If the coupling between the pair of states concerned, although more important than coupling to the other states, is nevertheless weak, the distorted wave

approximation discussed in Chapter 4 may be useful in particular cases.

Excitation of hydrogen and the close coupling method

The most extensive investigation of the excitation of the 2s and 2p state of hydrogen has been carried out within the close coupling approximation in the energy range between $n = 2$ threshold $(k^2 = 0.75)$ and the $n = 3$ threshold $(k^2 = 0.88)$, by Burke and his collaborators.[1] The explicit form of the wave function in the angular momentum representation, for total orbital angular momentum L, total spin S was:—

$$\Psi_{L,S}^{M_L} (\mathbf{r_1}, \mathbf{r_2}) = (1 + (-1)^S P_{12}) \left[\sum_{n, \ell_1, \ell_2} \left(\frac{1}{r_1 r_2}\right) R_{n\ell_1}(r_1) \times \right.$$

$$\times F_{n\ell_1 \ell_2}(r_2) Y_{L, \ell_1, \ell_2}^{M_L} (\theta_1 \varphi_1, \theta_2 \varphi_2) + \sum_i \frac{1}{r_1 r_2} \left(a_i e^{-\varkappa_1 r_1 - \varkappa_2 r_2} + \right.$$

$$\left. \left. + b_i e^{-\varkappa_1 r_2 - \varkappa_2 r_1} \right) r_1^{p_i} r_2^{q_i} r_{12}^{s_i} Y_{L, \ell_{1_i}, \ell_{2_i}}^{M_L} (\theta_1, \varphi_1; \theta_2, \varphi_2) \right]. \quad (6\text{-}11)$$

The first terms in square brackets represent the truncated eigenfunction expansion where $r_1^{-1} R_{n\ell_1}(r_1)$ are the radial functions for the state $(n\ell_1)$ of the hydrogen target and L, ℓ_1, ℓ_2 refer to the total angular momentum and that of the target and the incident electron, respectively. The second set of terms in the square brackets are of the algebraic type with parameters $a_i, b_i, \varkappa_i, p_i, q_i$ and s_i. Because of the dependence on the inter-electron distance r_{12}, these terms can represent correlation effects which are not explicitly included in the truncated eigenfunction expansion.

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[1] Burke et al. (1967a); Taylor and Burke (1967); Burke et al. (1967b); Macek and Burke (1967).

The functions

$$Y_{L,\ell_1,\ell_2}^{M_L}(\theta_1,\varphi_1; \theta_2,\varphi_2)$$

are the simultaneous eigenfunctions of the total orbital angular momentum L with Z component M_L and the orbital angular momentum of each electron, ℓ_1 and ℓ_2, We have in the usual notation that

$$Y_{L,\ell_1,\ell_2}^{M_L}(\theta_1,\varphi_1; \theta_2,\varphi_2) = \sum_{m_1,m_2} C_{\ell_1,\ell_2}(L,M_L,m_1,m_2) \times$$

$$\times Y_{\ell_1,m_1}(\theta_1,\varphi_1)\, Y_{\ell_2,m_2}(\theta_2,\varphi_2).$$

Provided the sum over the target eigenfunctions includes the 1s, 2s, and 2p states, the trial function satisfies the correct boundary conditions below the n = 3 threshold and the calculated sum of the eigenphases will represent a lower bound. Just below an excitation threshold resonances may exist, of the virtual bound state type. The resonance energies will be determined by the discrete spectrum of the closed channel Hamiltonian **QHQ** and it will be shown in the next chapter that the existence of a discrete spectrum is often connected with the long range forces, that are associated with degenerate thresholds. In the present case, to allow for possible resonances just below the n = 3 threshold, the closed 3s, 3p and 3d states should be included in the close coupling expansion. Below the discrete spectrum of (**QHQ**) there is no particular virtue in including the closed states explicitly, as algebraic terms of the Hylleraas type represent correlations between the electrons well, and it is comparatively easy to retain sufficient terms to obtain convergence. With these ideas in mind, Burke et al. have presented results in the six state (1s – 2s – 2p – 3s – 3p – 3d) approximation (Burke et al., 1967a) at energies above the n = 2 threshold, supplemented (Taylor and Burke, 1967) by calculations in the very narrow energy range $k^2 = 0.75$ to $k^2 = 0.85$ in which up to 20 correlation terms were used together with the 1s – 2s – 2p open channel terms, securing apparent convergence. The results in the six state and in the (3 state + correlation) approximations

agree satisfactorily. The correlation effects are not large and if only the three terms (1s - 2s - 2p) are retained, the cross section is within 15% of the most accurate values.

Below the n = 3 threshold the expected series of resonances are found. This can be seen clearly in Fig. 6-1 which shows the cross section $\sigma(1s - 2s)$, the cross section for excitation of the ground state to the (2s) state. Detailed analysis (Macek and Burke, 1967) shows that interference between resonant and non-resonant scattering controls the shape of the cross section in this region and is responsible for the peak observed in the 1s - 2s excitation cross section at 11.5 ev ($k^2 = 0.84$). Below the resonance region $k^2 < 0.84$, neither the explicit representation of the closed channels nor correlation is important and the 1s - 2s - 2p approximation is
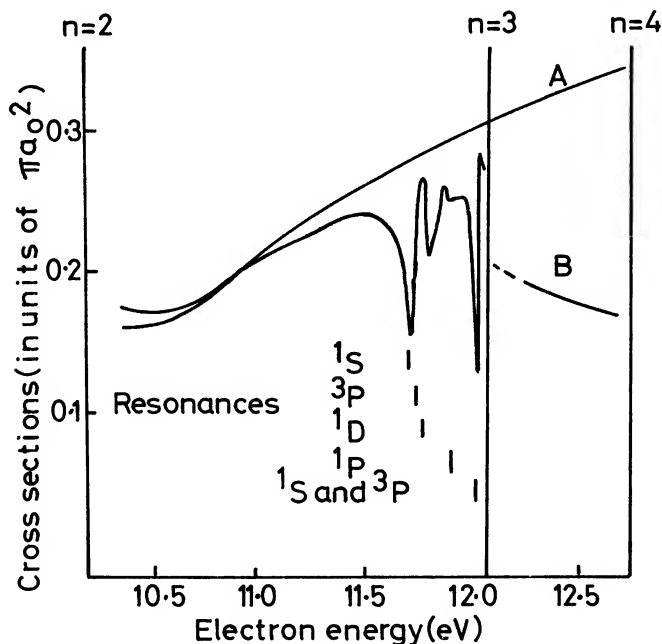
Figure 6-1.   The total cross section $\sigma(1s-2s)$ for the excitation of hydrogen by electron impact in the three-state (curve A) and the six-state (curve B) approximation (Burke et al., 1967a).

quite accurate. An interesting feature occurring in each app-
roximation is a narrow resonance (width 1.7×10^{-3} ev) just
above the n = 2 threshold in the ^1P state of the system.
Since this occurs in the (1s – 2s – 2p) approximation it has
nothing to do with the closed channels, but is a 'shape' reso-
nance of the kind observed in potential scattering and discussed
in Chapter 1.

    Measurements exist of both the cross section for
1s – 2s and for 1s – 2p excitation. The measurements of the
1s – 2s cross section are not absolute (Lichten and Schultz,
1959; Stebbings et al., 1960; Hills et al., 1966) but have
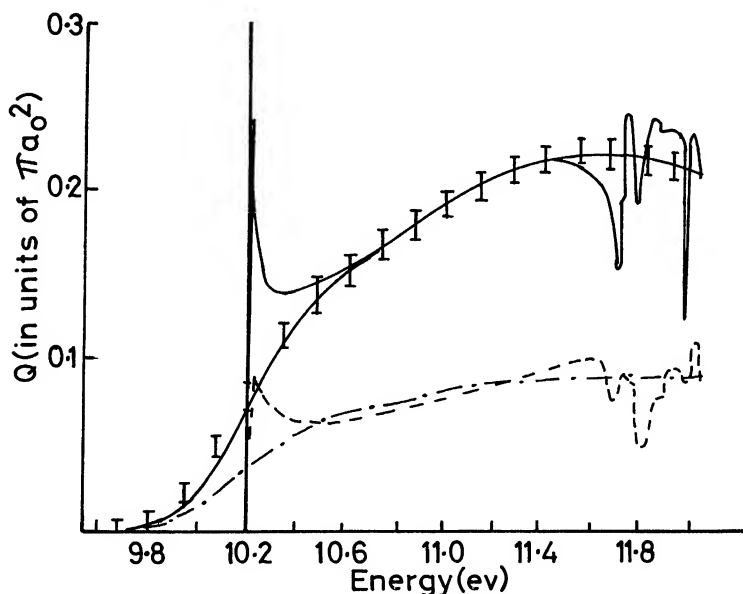
Figure 6-2.   The total and spin exchange cross sections for 1s-2s excitation of hydro-
gen by electron impact.

       ——————   Total cross section (close coupling calculations).

       — — —   Total cross sections folded with a beam of Gaussian shape and width
                 0.2 ev.

       —·—·—   Spin exchange cross section folded with Gaussian beam distribution.

         I   Experimental results of Lichten and Schultz (1959), normalized so
                 that the experimental and theoretical curves coincide at the maxi-
                 mum in the cross section (after Burke et al., 1967b).

been normalized to the Born cross sections at 300 ev. There is
considerable doubt whether such a normalization is adequate;
but if it is accepted, the theoretical and measured cross sec-
tions differ by a factor of 2. On the other hand, Lichten and
Schultz also measured the ratio of collisions in which the spin
of the target was reversed to those in which it was unaltered.
This spin exchange cross section can be calculated from the
theoretical cross sections and agrees very well with the experi-
ment (Fig. 6-2). The measurement of the 1s - 2s cross sec-
tions (Chamberlain et al., 1964; Fite et al., 1958, 1959) also
agree well with the theory. If the 1s - 2s experimental cross
sections are normalized to agree in magnitude with the theore-
tical cross sections, the shape of the cross sections is in
complete agreement with the theory (Burke et al., 1967b) and
it seems likely that the theoretical results are correct.

Calculations of excitation to the n = 3 level in hydro-
gen cannot be carried out without including the n = 4 states in
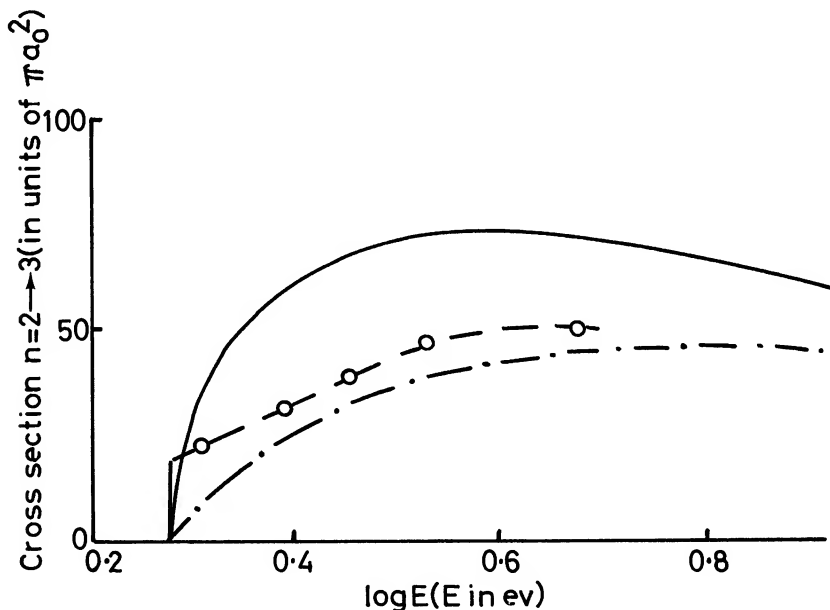
Figure 6-3. The total excitation cross section of hydrogen from the n = 2 levels to the
n = 3 levels by electron impact.

        ——— Born approximation.
      -o-o- Dipole approximation.
      —·—·— Six-state close coupling approximation (Burke et al., 1967a).

the close coupling expansion, because the coupling between
n = 3 and n = 4 level is strong. On the other hand, the coup-
ling between n = 2 and n = 3 levels is stronger than between
either of these levels and the n = 1 level. This suggests that if
the six state approximation is used above the n = 3 threshold
it should give reasonably accurate results for the n = 2 to
n = 3 transitions. The total cross section for excitation of the
n = 2 level, $\sigma(2 - 3)$,

$$\sigma(2 - 3) = \frac{1}{4} \sum_{\ell} \sigma(2s \to 3\ell) + \frac{3}{4} \sum_{\ell} \sigma(2p \to 3\ell), \qquad (6\text{-}12)$$

is shown in Fig. 6-3 and compared with the Born and dipole
approximations. The comparison will be discussed later.

Further applications

The close coupling method has also been applied to the
excitation of the n = 2 state in helium[2] and to transitions
among the n = 2 states[3]. Apart from the ground state of the
helium atom all four states with n = 2 ($2^3S, 2^1S, 2^3P, 2^1P$)
were included in the expansion. The $2^{3,1}S$ states have very
large polarizabilities because the $2^{3,1}P$ states are so close in
energy. The energies of the five states concerned are shown
in Table 6-1.

<div align="center">

Table 6-1

Binding energies of levels in helium with n = 2

</div>

State		E(a.u.)
2^1S	$1s^2$	2.9037
2^3S	$1s2s$	2.1754
2^1S	$1s2s$	2.1461
2^3P	$1s2p$	2.1333
2^1P	$1s2p$	2.1238

[2] Burke, Cooper and Ormonde (1966).

[3] Burke et al. (1967c).

The helium wave functions used in this work were of the Hartree-Fock type, and satisfactory agreement was obtained with the experimental data. The calculated cross sections show a resonant structure in the energy region below the thresholds.

The transitions between the ground state terms of carbon, nitrogen and oxygen due to electron impact are of considerable astronomical interest. As the ground state terms are strongly coupled this is also a favorable situation for the close coupling method and Smith et al. (1967) have calculated both the elastic cross sections and the inelastic transitions among the ground state terms of these atoms.

Calculations on the excitation of Li, Na, K and Cs (Karule and Peterkop, 1964, 1965) have been carried out on the basis, discussed earlier, that only the ground and first excited state are important because the first excited states contribute 98% of the polarizability. For calculational purposes the problem was simplified by only treating the incident and valence electrons explicitly. The effect of the remaining electrons and the nucleus was represented by an average (static) potential.

Ions

No particular difficulty occurs in extending the close coupling method to the scattering of electrons by ions. All that is necessary is to modify the form of the radial functions in the open channels so that they are asymptotic to linear corrections of the regular and irregular Coulomb functions (Chapter 3); for example,

$$f_{\ell}(r) \sim \delta_{a\gamma} F_{\ell}(k_a r) + K_{\gamma a} G_{\ell}(k_\gamma r). \tag{6-13}$$

The elastic scattering and excitation of the He^+ by electron impact has been considered in the 1s - 2s - 2p approximation by Burke et al. (1964a,b) and McCarrol (1964).

6-2   BORN'S APPROXIMATION

It is not feasible to carry out the elaborate calculations of the eigenfunction expansion method for all the transitions of interest, but several alternative procedures may provide accurate results under certain circumstances. At high energies the Born approximation is expected to be valid for direct collisions

and has been used widely. For total cross sections the agree-
ment between the calculated and experimental cross sections
is close for electron   energies 10 times the threshold energy
of the transition concerned, and as a consequence (Peterkop and
Veldre, 1966) the Born approximation is valid at above an inci-
dent energy of 10 ev for excitation of atoms from higher states
and above about 100 ev for excitation from the ground state.

As exchange effects decrease rapidly as the energy of
the incident electron increases, we shall not at first take into
account the identity of the electrons. This implies that colli-
sions in which the spin of the target changes (for example,
excitation of the triplet states of helium from the ground states)
which, in the absence of spin dependent potentials, take place
purely through electron exchange,will be excluded from our dis-
cussion. The Born approximation for the total cross section is
given by (4-26) together with (4-41). The unperturbed wave
functions are of the form (4-7) (with $N_\gamma = 1$) and,

$$\sigma_{nm}(E) = \frac{1}{4\pi^2} \frac{k_n}{k_m} \int d\Omega |T_{nm}|^2, \qquad (6\text{-}14)$$

with

$$T_{nm} = \int d\mathbf{r} \int d\mathbf{x}\, X_n^*(\mathbf{x}) e^{-i\mathbf{k}_n \cdot \mathbf{r}} V(\mathbf{r},\mathbf{x}) X_m(\mathbf{x}) e^{i\mathbf{k}_m \cdot \mathbf{r}}. \qquad (6\text{-}15)$$

In these formulae atomic units are employed and the channel
label has been dropped, the transition being determined by the
initial and final states of the targets m and n with eigen-
functions X_m and X_n.

Conservation of energy requires that

$$\frac{1}{2} k_n^2 + \epsilon_n = \frac{1}{2} k_m^2 + \epsilon_m, \qquad (6\text{-}16)$$

where ϵ_i is the energy of the ith state of the target. The
interaction, $V(\mathbf{r},\mathbf{x})$, between the incident electron and the
target is of the form

$$V(\mathbf{r},\mathbf{x}) = \frac{Z}{r} - \sum_{i=1}^{Z} \frac{1}{|\mathbf{r} - \mathbf{x}_i|}. \qquad (6\text{-}17)$$

The first term represents the interaction of the incident electron with the nucleus of the target and the second the interaction with each of the electrons in the target (coordinates $x_1, x_2 \ldots x_Z$). The orthogonality of the wave functions X_m and X_n for $m \neq n$, insures that the contribution of the first term vanishes except for elastic scattering.

Elastic scattering

Absolute measurements of elastic scattering cross sections are not available to test the predictions of the Born approximation.[4] If the observed cross sections are normalized to the Born approximation at some high energy, the consistency of the observed and calculated angular distributions can be checked at different energies. In Fig. 6-4, the differential
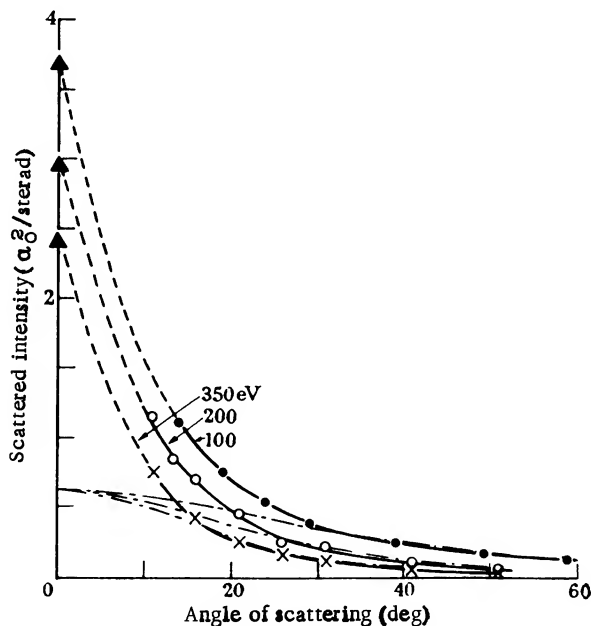
Figure 6-4. Angular distribution of elastically scattered electrons from helium atoms from 100-350 ev.

▲   Zero angle limit determined from the forward dispersion relations.
—·—·— Calculated by the Born approximation (after Lawson et al., 1966).

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[4] See note on page 282.

cross sections measured by Hughes et al. (1932), for the elastic scattering of electrons by helium atoms over an angular range of from 10° to 147° are shown for incident energies of 100, 200 and 350 ev. These results were normalized to agree with the Born approximation at 700 ev. The agreement between the experiments and the Born approximation is good for angles greater than 30° at 100 ev and greater than 18° at 350 ev. In the forward direction the differential cross section can be calculated from the dispersion relations, discussed in the last chapter, and these calculated points are shown in Fig. 6-4. It is seen that the dispersion relation points fall in a natural extrapolation of the observed cross sections, but disagree considerably with the predictions of the Born approximation. The forward scattering amplitude is complex with an imaginary part that is determined by the optical theorem in terms of the total cross section. It follows that as the amplitude given by the Born approximation is real, the Born approximation must fail near the forward direction, although the range of angles for which it fails decreases with increasing energy. In general the total cross section given by the Born approximation can be quite accurate, even if the angular distribution is poorly represented in the forward direction.

For heavier atoms, the interaction is stronger, being proportional to Z, so that the energy above which the Born approximation is accurate becomes greater; for example, reasonable accuracy is not expected for scattering by argon and neon until the energy exceedes 1000 ev (Mott and Massey (1965), page 466).

Inelastic scattering

It is convenient to use the momentum transfer K

$$\mathbf{K} = \mathbf{k}_m - \mathbf{k}_n, \tag{6-18}$$

as a variable in place of the angle of scattering θ. Since

$$K^2 = k_n^2 + k_m^2 - 2k_n k_m \cos \theta,$$

the total cross section can be written as

$$\sigma_{nm}(E) = \left(\frac{1}{2\pi k_m^2}\right) \int_{K_{min}}^{K_{max}} |T_{nm}(K)|^2 K \, dK, \tag{6-20}$$

where $K_{max} = k_m + k_n$ and $K_{min} = k_m - k_n$, and

$$T_{nm}(K) = -\sum_{i=1}^{Z} \int d\mathbf{r} \int d\mathbf{x}\, X_n^*(\mathbf{x}) X_m(\mathbf{x})\, \frac{e^{i\mathbf{K}\cdot\mathbf{r}}}{|\mathbf{r} - \mathbf{x}_i|}. \qquad (6\text{-}21)$$

In (6-21), $\mathbf{x}_i$ is the position vector of the ith electron, and as usual $\mathbf{x}$ denotes the coordinates of all the target electrons collectively.

When the change in energy of the target $(\epsilon_m - \epsilon_n)$ is small compared with the incident momentum, it is a good approximation to set

$$K_{max} = 2k_m,$$

$$K_{min} = \left(\frac{\epsilon_n - \epsilon_m}{k_m}\right) = \left(\frac{k_m^2 - k_n^2}{2k_m}\right). \qquad (6\text{-}22)$$

The expression (6-21) for $T_{nm}(K)$ can be simplified by using the result,

$$\int \frac{1}{|\mathbf{r} - \mathbf{x}_i|} e^{i\mathbf{K}\cdot\mathbf{r}}\, d\mathbf{r} = e^{i\mathbf{K}\cdot\mathbf{x}_i} \lim_{\lambda \to 0} \int \frac{1}{y} e^{i\mathbf{K}\cdot\mathbf{y}} e^{-\lambda y}\, d\mathbf{y}$$

$$= \frac{4\pi}{K^2} e^{i\mathbf{K}\cdot\mathbf{x}_i}.$$

We obtain

$$\frac{K^2}{4\pi} T_{nm}(K) = -\sum_{i=1}^{Z} \int d\mathbf{x}\, X_n^*(\mathbf{x}) X_m(\mathbf{x})\, e^{i\mathbf{K}\cdot\mathbf{x}_i}. \qquad (6\text{-}23)$$

It is usual to write the cross section in terms of a generalized oscillator strength defined as

$$f_{nm}(K) = 2(\epsilon_n - \epsilon_m)\, |T_{nm}(K)|^2 K^2, \qquad (6\text{-}24)$$

so that the total cross section for excitation of the nth state of the atom from the mth state is

$$\sigma_{nm}(E) = \frac{1}{4\pi} \frac{1}{(\epsilon_n - \epsilon_m)k_m^2} \int_{K_{min}}^{K_{max}} \frac{f_{nm}(K)}{K}\, dK. \qquad (6\text{-}25)$$

The generalized oscillator strength becomes equal, in the limit $K \to 0$, to the optical oscillator strength $f_{nm}(0)$ which is proportional to the probability of an optical transition between the m and nth level of the target.

The case of most interest is when the target is initially in the ground state $(m = 0)$. It can then be shown (Mott and Massey, 1961, p. 479) that the oscillator strengths obey the sum rule,

$$\sum_n f_{no}(K) = 1,$$

where the sum is over all states (discrete and continuous) of the target atom.

A multipole expansion of $f_{no}(K)$ can be performed by expanding the exponential in (6-21) in a Taylor's series. Taking $\mathbf{K}$ to be in the direction of the x axis,

$$f_{no}(K) = 2(\epsilon_n - \epsilon_o)(4\pi)^2 \left| i(X_n | \sum_{i=1}^{Z} x_i | X_0) + \right.$$

$$\left. + (i)^2 \frac{K}{2}(X_n | \sum_{i=1}^{Z} x_i^2 | X_0) + \ldots \right|^2, \quad n \neq 0, \quad (6\text{-}27)$$

where

$$(X_n | \mathbf{O} | X_m) \equiv \int d\mathbf{x}\, X_n^*(\mathbf{x})\, \mathbf{O}\, X_m(\mathbf{x}),$$

showing that, as $K \to 0$, $f_{no}(K)$ is proportional to the square of the matrix element of the atomic dipole moment. The differential cross section $(d\sigma_{no}/dK)$ is a slowly decreasing function of K, because at high energies the scattering is entirely concentrated in a forward direction (see Chapter 1). It follows that for optically allowed transitions $(\Delta\ell = 1)$, the most important term in the expansion will be the dipole term and approximately (using 6-22)

$$\sigma_{no} = \frac{8\pi}{k_o^2} \left| (X_n | \sum_{i=1}^{Z} x_i | X_0) \right|^2 \log\left(\frac{4k_o^2}{k_o^2 - k_n^2}\right). \quad (6\text{-}28)$$

This is the Bethe approximation which becomes exact in the high energy limit. If the dipole matrix element vanishes, the quadrupole $(\Delta\ell = 0, 2)$ term in the expansion will provide a

corresponding approximation. It is important to notice that while the cross sections for the optically allowed transitions fall off as $k_0^{-2} \log (k_0^2)$ as k_0 increases, those for quadrupole and higher transitions decrease like k_0^{-2}. The Bethe approximation is important in developing the theory of the stopping power of materials to fast charged particles.

Validity of Born approximation

An experimental check on the validity of the Born approximation is possible. If the quantity

$$f(K) = 2\pi k_0^2 (k_0^2 - k_n^2) K \left(\frac{d\sigma_{no}}{dK}\right) \qquad (6-29)$$

is constructed from the measured cross section, $(d\sigma_{no}/dK)$, then, if the Born approximation holds, $f(K)$ should depend on K but not on the incident energy $(k_0^2/2)$ and will equal the theoretical oscillator strength $f_{no}(K)$. Measurements of $(d\sigma_{no}/dK)$ have been carried out by Lassetre and his collaborators[5] for excitation of the $2^1S, n^1P$ states in helium with $n \leq 5$. They find the Born approximation is well satisfied for energies greater than 400 ev. The shape of the function $f(K)$ for the $1^1S \to 2^1P$ transition also agrees well with theoretical calculations of Lassetre and Jones (1964) although of course this is a test of the accuracy of the helium wave functions used as well as of the validity of the Born approximation.

Differential and total cross sections for the excitation of the 2^1P and 2^1S states have also been measured by Vriens et al. (1968) for electron energies between 100 and 400 ev. The measured $f(K)$ is shown in Fig. 6-5 for the transition $1^1S \to 2^1P$. It is seen that for this transition the Born approximation holds down to 100 ev, but for the $1^1S \to 2^1S$ transition departures from the Born approximation are fairly marked below 300 ev.

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[5] Lassetre and Silverman (1964); Lassetre et al. (1964).
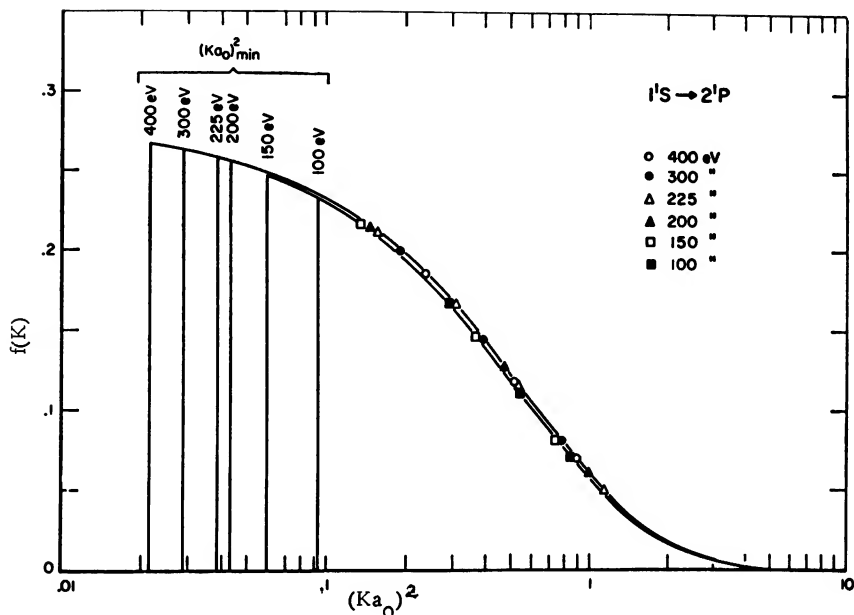
Figure 6-5.   Apparent generalized oscillator strengths for the excitation of helium to the 2^1P state from the ground state, by electron impact.   The solid lines represent a fit to the data with the form

$$f(K) = f(0)(1 + x)^{-6} \left\{ 1 + \sum_n C_n \left(\frac{x}{1 + 2} \right)^2 \right\},$$

where $x = (Ka_0/a)^2$, $a^2 = 3.391$, $f(0) = 0.27616$

(Vriens et al., 1968).

It is interesting to notice that if measurements are made at high energies, for which the minimum value of K^2 is small, it is possible to obtain accurate values of the optical oscillator strengths $f_{no}(0)$, by extrapolating the measurements to $K = 0$.

Scattering or excitation of charged ions can be treated in the Coulomb-Born approximation by replacing the plane waves in the transition matrix (6-15) by Coulomb functions appropriate to the charge on the ion.   We have in place of (6-15)

$$T_{nm} = \int d\mathbf{r} \int d\mathbf{x} X_m^*(\mathbf{x}) \left(\psi_{\mathbf{k}_m}^{C^-}(\mathbf{r}) \right)^* V(\mathbf{r}, \mathbf{x}) X_n(\mathbf{x}) \psi_{\mathbf{k}_n}^{C^+}(\mathbf{r}), \quad (6\text{-}30)$$

and it is important to notice that $(\psi^-)^*$ must be used to des-
cribe the final state in order to conform to the correct boundary
conditions. The threshold law for excitation of ions differs
from that of neutral atoms. In the latter case, the cross sec-
tion is controlled by the behavior of the lowest ($\ell = 0$) partial
wave and variables at threshold. This is not the case for the
excitation of positive ions and from the behavior of $\psi_{\mathbf{k}_m}^{-*}$ for

small (kr) it can be shown that T_{nm} is proportional to $k_m^{-1/2}$
so that $\sigma_{nm}(E)$ approaches a non-zero value at threshold.
Tully (1960) has obtained cross sections in this approximation
for the 1s - 2s transition in the hydrogen iso-electronic
sequence and Burgess (1961) has extended this work to the
1s - 2p transitions. For sufficiently large values of the in-
cident energy, the Coulomb waves may be replaced by plane
waves, then if the cross sections σ_{nm} are expressed as a

function of $w = k_m^2/(k_m^2 - k_n^2)$, the quantity $Z^4 \sigma_{nm}(w)$ will be
independent of Z. Calculations show that this is true for
$w > 3$ and that at high energies the cross sections are inversely
proportional to Z^4.

A large number of calculations in the Born approximation
have been carried out, particularly for the transitions between
highly excited levels which are of interest in plasma physics
and in astrophysical applications. The literature may be traced
from the review by Peterkop and Veldre (1966).

6-3 THE BORN APPROXIMATION AT LOWER ENERGIES

At high energies the partial cross sections for all ℓ
will be small and each will be determined accurately by the
Born approximation. At lower energies, the partial cross sec-
tion for large ℓ may still be given accurately by the Born
approximation, but those for small ℓ, for which the scattering
is large, will be in error. When the scattering is strong in a
given partial wave the unitarity limit is often exceeded by the
Born approximation. Under these circumstances, a much better
approximation is obtained by evaluating the **K** matrix elements,
for each partial wave, rather than the **T** matrix elements, since
if the **S** matrix is constructed from the **K** matrix the result
always satisfies the unitarity restrictions. In addition, if the
K matrix elements are available in the plane wave approximation

for each transition connecting a number of states, the corresponding S matrix, where $S = (1 + iK)/(1 - iK)$ will contain some allowance for the effects of coupling between the channels, which is entirely omitted in the usual Born approximation. The Born approximation for the reaction matrix has been discussed by Seaton (1961) and applied to the discussion of the excitation of the 2s and 2p states of hydrogen by Burke and Seaton (1961) (see also Lawson et al., 1961). The results are an improvement over those of the simple Born approximation and are illustrated in Fig. 6-6 for the 1s → 2p transition.
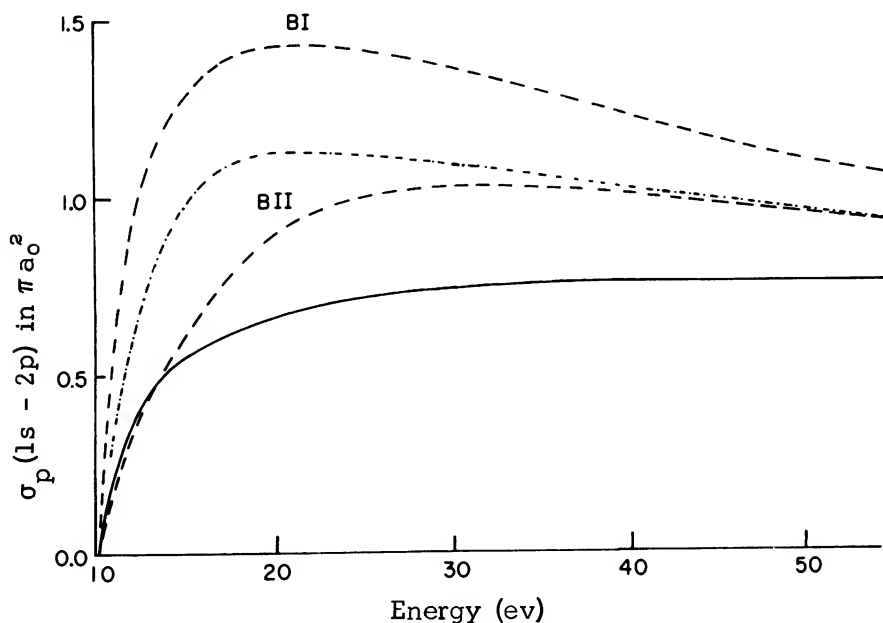
Figure 6-6.   The cross section for photons emitted perpendicular to the beam, σ_p
after the 1s-2p excitation of hydrogen by electron impact.

———   Experimental results of Fite et al. (1959).

- - - - -   Unitary versions of the Born approximation (Burke and Seaton, 1961),

$$S_{BI} = 1 + 2iK_B, \qquad S_{BII} = \left(\frac{1 + iK_B}{1 - iK_B}\right).$$

- - - - -   Exchange distorted wave approximation (Khashaba and Massey, 1958).

The second Born approximation

At lower energies when the first Born approximation is less accurate, better results should be obtained if the next term in the perturbation series is evaluated. The sum of the first two terms in the series is known as the second Born approximation. In this approximation the distortion of the atom by the field of the incident particle is taken into account. The transition matrix element is now given by

$$T_{nm} = T_{nm}^{\ 1} + T_{nm}^{\ 2},\tag{6-31}$$

where $T_{nm}^{\ 1}$ is the first Born approximation to T_{nm} given by (6-15) and $T_{nm}^{\ 2}$ is defined by

$$T_{nm}^{\ 2} = 2 \sum_i \int d\mathbf{r} \int d\mathbf{r}' \left[e^{-i\mathbf{k}_n \cdot \mathbf{r}} V_{ni}(\mathbf{r}) \frac{e^{ik_i|\mathbf{r} - \mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|} V_{im}(\mathbf{r}') e^{i\mathbf{k}_m \cdot \mathbf{r}'} \right]\tag{6-32}$$

where we have used the Green's function of equation (4-45) and

$$V_{ij}(\mathbf{r}) = (X_i | V(\mathbf{r},\mathbf{x}) | X_j).\tag{6-33}$$

The sum over i is over all the states of the target atom including the continuum states. It is clear that an exact evaluation of $T_{nm}^{\ 2}$ is impossible, however. Several approximate methods have been devised and tested in the case of electron hydrogen atom scattering. One possibility (Massey and Mohr, 1934) is to ignore the variation of k_i occurring in the free particle Green's function. If k_i is set equal to k_m, then the closure of the atomic wave functions X_i, $(\sum_i |X_i)(X_i| = 1)$, can be used to effect the sum over i. We find

$$T_{nm}^{\ 2} \simeq 2 \int d\mathbf{r} e^{-i\mathbf{k}_n \cdot \mathbf{r}} M(\mathbf{r},\mathbf{r}') \frac{e^{ik_m|\mathbf{r} - \mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|} e^{i\mathbf{k}_m \cdot \mathbf{r}'},\tag{6-34}$$

where

$$\begin{aligned}
M(\mathbf{r},\mathbf{r}') &= \sum_j \left(X_n | V(\mathbf{r},\mathbf{x}) | X_j \right)\left(X_j | V(\mathbf{r}',\mathbf{x}) | X_m \right) \\
&= \left(X_n | V(\mathbf{r},\mathbf{x}) V(\mathbf{r}',\mathbf{x}) | X_m \right).
\end{aligned}\tag{6-35}$$

$T_{nm}{}^2$ can be evaluated analytically in this approximation in the case of electron hydrogen atom scattering.

An alternative approach (Kingston and Skinner, 1961; Moiseiwitsch and Perrin, 1965) is to calculate the first few terms in the sum over i and ignore the remainder. By carrying a sufficient number of terms, this procedure probably converges reasonably rapidly as far as the discrete atomic states are concerned, but it fails to make any allowance for the continuum states. A recent investigation by Holt and Moiseiwitsch (1968) combines the advantages of both approaches to the problem. They calculate the first few terms of the sum (for i = 1 to i = n) exactly and the remainder is calculated in the closure approximation by setting $k_i = k_N, i > N$. As the contribution from terms with i > N is quite small (< 10%), the results are expected to be accurate.

If the cross section σ_{nm} is required to a given order in e^2, where e is the electronic charge, care must be taken to be consistent. For example, if $[T^1 + T^2]$ is used as it stands, all terms up to and including $(e^2)^3$ will be included, but only some of the terms in $(e^2)^4$. Including all terms up to $(e^2)^3$ but omitting terms in $(e^2)^4$ we have

$$|T|^2 \simeq |T^1|^2 + 2T^1 \mathrm{Re} T^2. \qquad (6-36)$$

It is in this approximation that Holt and Moiseiwitsch have calculated their results. Although this provides an approximation to σ_{nm} which is consistently calculated up to terms of order $(e^2)^3$, the approximation still fails to satisfy unitarity because the imaginary part of the amplitude, $\mathrm{Im} T^2$, is ignored as it contributes to order $(e^2)^4$. Cross sections for the elastic scattering and for the excitation of the 2s and 2p levels, have been calculated by Holt and Moiseiwitsch for both electron and proton impact on atomic hydrogen. In Table 6-1 the results for 1s - 2s excitation by electron impact are illustrated.

It is clear that at higher energies the results converge rapidly with increasing N, and that the first Born approximation appears to be accurate to better than 10% for all energies greater than $k^2 = 9$ (~122 ev), but is beginning to fail at $k^2 = 4$ (~54 ev). The corresponding results for proton impact show substantial deviations from the first Born approximation

Table 6-1

Cross section for 1s - 2s excitation of hydrogen by electron impact

(Units of πa_o^2)

k^2(a.u.)	First Born approximation	Second Born approximation				
		N = 1	2	3	4	5
4	0.1019	0.103	0.0873	0.0837	0.0822	0.0814
9	0.0476	0.0476	0.0452	0.0447	0.0444	0.0443
16	0.0272	0.0271	0.0266	0.0265	0.0264	0.0264
25	0.0175	0.0174	0.0173	0.0173	0.0173	0.0173

for 1s - 2s excitation even at several hundred kev. For 1s - 2p excitation the Born approximation holds down to lower energies than for the 1s - 2s transition, being less than 10% in error at 50 ev for electron impact.

The dipole approximation

The Born approximation fails at lowest energies, at first, for states with small values of orbital angular momentum (see Chapter 1). A semi-empirical method introduced by Seaton (1961) attempts to correct for this defect by removing the lower partial waves and replacing them by a parameter. The approximation is conveniently expressed in an impact parameter formulation, remembering that small values of the angular momentum correspond to small values of the impact parameter b.

For impact parameters b > a, where a is the range of the atomic interaction, the incident electron is not expected to be deflected significantly, and, provided that (kb) $\gg$ 1, the motion of the electron is specified by the straight line classical trajectory

$$\mathbf{r}(t) = \mathbf{v}t + \mathbf{b} ,$$
(6-37)

$$\mathbf{b} \cdot \mathbf{v} = 0,$$

where the nucleus of the atom is taken as the origin of the coordinate system. The z axis is taken to be parallel to the velocity of the electron $\mathbf{v}$, where $\mathbf{v} = \hbar\mathbf{k}/m$ and t = 0 is the time of closest approach.

The time dependent wave function $\Psi(\mathbf{x},t)$ of the target atom in the field of the incident electron, satisfies

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{x},t) = [H_0(\mathbf{x}) + V(\mathbf{x},t)]\Psi(\mathbf{x},t), \qquad (6-38)$$

where $H_0(\mathbf{x})$ is the Hamiltonian of the unperturbed atom. For electron hydrogen scattering we have (in atomic units)

$$i\frac{\partial \Psi}{\partial t} = \left[-\frac{1}{2}\nabla_x^2 - \frac{1}{x} - \frac{1}{r(t)} + \frac{1}{|\mathbf{r}(t) - \mathbf{x}|} \right]\Psi. \qquad (6-39)$$

The complete wave function $\Psi(\mathbf{x},t)$ can be expanded in terms of the orthonormal eigenfunctions $\varphi_n(\mathbf{x})$ of H_0:

$$\Psi(\mathbf{x},t) = \sum_{n=0}^{\infty} a_n(t)\varphi_n(\mathbf{x}) e^{-i\epsilon_n t/\hbar}, \qquad (6-40)$$

where ϵ_n is the energy of the state n. And by substitution into equation (6-38), multiplying by $\varphi_n^*(\mathbf{x})$ and integrating over $\mathbf{x}$ we find coupled equations for the coefficients $a_n(t)$:—

$$i\hbar \frac{da_n}{dt} = \sum_m V_{nm}(t)a_m(t) e^{i(\epsilon_n - \epsilon_m)t/\hbar}, \qquad (6-41)$$

where the potential matrix $V_{nm}(t)$ is defined by

$$V_{nm}(t) = \int \varphi_n^*(\mathbf{x})V(\mathbf{x},t)\varphi_m(\mathbf{x})d\mathbf{x}. \qquad (6-42)$$

If the initial state of the atom is the ith state, then as $t \to -\infty$ we must impose the boundary conditions,

$$a_i(-\infty) = 1,$$

$$a_j(-\infty) = 0, \quad j \neq i. \qquad (6-43)$$

Then, to first order,

$$a_j(t) = \frac{1}{i\hbar} \int_{-\infty}^{t} V_{ji}(t) e^{i(\epsilon_j - \epsilon_i)t/\hbar} dt. \qquad (6-44)$$

The transition probability for the transition $i \to j$ is then

$P_{ji} = |a_j(\infty)|^2$ and the corresponding cross section is

$$\sigma_{ji}(E) = 2\pi \int_0^\infty P_{ji}(b) b\, db. \tag{6-45}$$

If we are interested in excitation of a group of degenerate levels from a degenerate level, we must sum over the final states and average over the initial states, giving

$$\sigma_{ji}(E) = \frac{2\pi}{w_i} \int_0^\infty P_{ji}(b) b\, db, \tag{6-46}$$

where w_i is the statistical weight of the level i.

An approximation (compare the Bethe approximation) can be introduced by replacing $V(\mathbf{r}(t), \mathbf{x})$ by its asymptotic form for large $|\mathbf{r}|$, which is consistent with the condition that $b > a$. For optically allowed transitions the leading term is the dipole term and (for hydrogen)

$$V_{nm}(t) \simeq -\frac{\mathbf{r}(t)}{r^3(t)} \int \varphi_n^*(\mathbf{x}) \mathbf{x} \varphi_m(\mathbf{x}) d\mathbf{x}. \tag{6-47}$$

Then, using (6-27), we find that

$$P_{ji}(b) = a(b) \frac{3 f_{ij}(0)}{k_j^2 - k_i^2}, \tag{6-48}$$

where

$$a(b) = \frac{1}{(4\pi)^2} \frac{1}{3} \left| \int_{-\infty}^\infty e^{it(\epsilon_j - \epsilon_i)} \frac{\mathbf{r}(t)}{r^3(t)} dt \right|^2.$$

The integral $a(b)$ reduces to (atomic units)

$$a(b) = \frac{4}{3} \frac{\beta^2}{(bk)^2} \left[K_0^2(\beta) + K_1^2(\beta) \right], \tag{6-50a}$$

where K_0 and K_1 are modified Bessel functions and

$$\beta = \frac{b}{k}(\epsilon_j - \epsilon_i). \tag{6-50b}$$

If the levels are degenerate the factor w_i is included in the definition of $f_{ji}(0)$,

$$f_{ji}(0) = \frac{1}{3w_i} \left| \int \varphi_j^*(\mathbf{x})x\varphi_i(\mathbf{x})d\mathbf{x} \right|^2 .$$

For small b, $\alpha(b)$ is divergent and a cut-off is introduced into the theory by replacing the lower limit of the integration over b in (6-45), by a finite value b_0.

$$\sigma_{ji} = 2\pi \int_{b_0}^{\infty} bP_{ji}(b)\, db. \tag{6-51}$$

The value of b_0 is determined by requiring that σ_{ji} coincides with the usual Born approximation in the high energy limit.

   This simple approximation gives more accurate cross sections than the Born approximation except close to the threshold (Seaton, 1962; Saraph, 1964; Burgess, 1964). It has been successfully extended to quadrupole transitions $(\Delta\ell = 2)$ by Stauffer and McDowell (1965). In Fig. 6-3, the dipole and Born results for the transition 2s - 3s are shown in relation to those in the close coupling method. This is an interesting example because although the dipole method agrees with elaborate calculations the agreement must be accidental, since the coupling between the states included in the eigenfunction expansion is far from small.

6-4   THE DISTORTED WAVE AND IMPULSE APPROXIMATION

   The basis of the distorted wave approximation has been discussed in Chapter 4. It may be applied to any coupled equations connecting a pair of states and is valid if the coupling is weak. There is no difficulty in including exchange effects. In general the Born approximation cross sections are too large at low energies and the distorted wave approximation is often quite effective in reducing the cross sections to about the right order of magnitude. A very different form of distorted wave approximation has been introduced by Vainshtein et al. (1964), in which instead of allowing for the average static interaction in the incident and final channel, an attempt is made to allow fully in the wave function for the repulsion between the electrons.

   For electron hydrogen atom system, the Schrödinger equation is

$$\left\{-\frac{1}{2}\nabla_r^2 - \frac{1}{2}\nabla_x^2 - \frac{1}{x} - \frac{1}{r} + \frac{1}{|\mathbf{x} - \mathbf{r}|} - E\right\}\Psi(\mathbf{x},\mathbf{r}) = 0, \quad (6-52)$$

where $\mathbf{x}$ is the position vector of the atomic and $\mathbf{r}$ of the incident electron. If the electron is incident on the ground state of hydrogen, we write

$$\Psi(\mathbf{x},\mathbf{r}) = \varphi_0(x)g(\mathbf{x},\mathbf{r}). \qquad (6-53)$$

The transition matrix element T_{n0} is then

$$T_{n0} = \int d\mathbf{r} \int d\mathbf{x}\, e^{-i\mathbf{k}_n \cdot \mathbf{r}} \varphi_n(x)V(\mathbf{x},\mathbf{r})\varphi_0(x)g(\mathbf{x},\mathbf{r}), \quad (6-54)$$

where

$$V(\mathbf{x},\mathbf{r}) = \frac{1}{|\mathbf{x} - \mathbf{r}|} - \frac{1}{r}.$$

This is exact, but if g were replaced by the plane wave $\exp(i\mathbf{k} \cdot \mathbf{r})$ the Born approximation would be regained. By substituting the form (6-53) into the Schrödinger equation, an equation for $g(\mathbf{x},\mathbf{r})$ is obtained. In terms of the variables $\boldsymbol{\rho} = 1/2(\mathbf{r} - \mathbf{x})$ and $\mathbf{R} = 1/2(\mathbf{r} + \mathbf{x})$, which describe the relative motion of the two electrons and the motion of the center of mass respectively, this equation is

$$\left[\frac{1}{2}\nabla_R^2 + \frac{1}{2}\nabla_\rho^2 + \frac{1}{R} - \frac{1}{\rho} + k_0^2\right]g(\mathbf{R},\boldsymbol{\rho}) = Hg(\mathbf{R},\boldsymbol{\rho}), \quad (6-55)$$

where H is the operator

$$H = \left\{\frac{1}{R} - \frac{2}{|\mathbf{R} + \boldsymbol{\rho}|} - (\boldsymbol{\nabla}_r \log \varphi_0) \cdot (\boldsymbol{\nabla}_R \log g - \boldsymbol{\nabla}_\rho \log g)\right\}$$

The approximation now consists in dropping the term Hg on the right hand side of (6-55). The function g is then of the form of the product of two Coulomb functions,

$$g(\mathbf{R}, \boldsymbol{\rho}) = Ne^{i\mathbf{k} \cdot (\mathbf{R}+\boldsymbol{\rho})}F(ik^{-1}, 1, ikR - i\mathbf{k} \cdot \mathbf{R}) \times$$

$$\times F(-ik^{-1}, 1, ik\rho - i\mathbf{k} \cdot \boldsymbol{\rho}), \qquad (6-56)$$

where $N = \Gamma(1 - ik^{-1})\Gamma(1 + ik^{-1})$. The first factor describes the motion of the center of mass of the two electron systems in the field of the nucleus and the second describes the interaction of the two electrons. The normalization is such that

the correct scattering boundary conditions are satisfied. With
this approximation for g, the transition matrix element can
be evaluated, partly analytically and partly numerically. The
justification for the approximation is that it allows completely
for the interaction of the two electrons and this is the inter-
action responsible for the excitation. The method may be ex-
tended to allow for exchange and by introducing an effective
charge some allowance for the discarded terms in the equation
can be made. For the 1s - 2s excitation of hydrogen by elec-
tron impact, the numerical results (Crowthers and McCarroll,
1965) are quite close to those given by the close coupling
method, but it is not clear whether this agreement is more
than accidental.

The method is similar in some ways to the impulse
approximation, which also attempts to account for the electron-
electron interaction. This is essentially a high energy app-
roximation, in which it is assumed that, during the short period
of interaction of the projectile with the target, the interaction
between the bound particles may be neglected. It is also
assumed that the projectile only interacts with one particle in
the target at a time, so that the scattering amplitude is a sum
of amplitudes for two particle scattering. To illustrate this
idea we shall consider electron–hydrogen atom scattering, and
we will take into account only the interaction between the
electrons 1 and 2. If the bound electron were a free particle
with momentum $\mathbf{p}$, then the wave function describing the
interaction between the two electrons would be $\Psi_{\mathbf{p},\mathbf{k}}(\mathbf{r}_1,\mathbf{r}_2)$,

where

$$\Psi_{\mathbf{p},\mathbf{k}}(\mathbf{r}_1,\mathbf{r}_2) = \exp\left[i(\mathbf{p}+\mathbf{k})\cdot\frac{1}{2}(\mathbf{r}_1+\mathbf{r}_2)\right]\psi_{\mathbf{q}}^{c^+}(\mathbf{r}_1-\mathbf{r}_2),$$

$$(6\text{-}57)$$

and

$$\mathbf{q} = \frac{1}{2}(\mathbf{p}-\mathbf{k}).$$

The first factor describes the motion of the center of mass of
the two electrons and the second the Coulomb scattering of
the two electrons in their center of mass system:

$$\psi_{\mathbf{k}}^{c^+}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}\Gamma\left(1+\frac{i\alpha}{2K}\right)e^{-\alpha\pi/4k}{}_1F_1\left(-\frac{i\alpha}{4k},1,ikr-i\mathbf{k}\cdot\mathbf{r}\right).$$

Because the target electron is bound, it will possess a momentum distribution determined by the Fourier transform $\widetilde{\varphi}_0(\mathbf{p})$ of the hydrogen atom ground state wave function. The wave function for the complete system $\Psi_I(\mathbf{r}_1, \mathbf{r}_2)$ is then obtained by averaging $\Psi_{\mathbf{p},\mathbf{k}}(\mathbf{r}_1, \mathbf{r}_2)$ over this distribution.

$$\Psi_I(\mathbf{r}_1, \mathbf{r}_2) \simeq \int d\mathbf{p}\, \widetilde{\varphi}_0(\mathbf{p}) \Psi_{\mathbf{p},\mathbf{k}}(\mathbf{r}_1, \mathbf{r}_2).$$

The approximate wave function Ψ_I can now be employed to calculate the transition matrix element T_{n0},

$$T_{n0} = \int \varphi_n^*(r_1) e^{-i\mathbf{k}_n \cdot \mathbf{r}_2} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \Psi_I(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2.$$

This approximation for electron scattering was originally introduced by Akerib and Borowitz (1961), but they made further approximations when evaluating T_{n0} which may not be valid. These approximations are avoided in the work of Coleman (1968) and Coleman and Trelease (1968), who examined the scattering of protons by hydrogen, for which the assumption that the interaction between the projectile and the nucleus may be neglected can be justified, but it is not at present clear whether the method can be considered successful in treating atomic problems. Corrections to the impulse approximation may be developed and details may be found in the papers by Ashkin and Wick (1952) and Chew and Wick (1952).

Unlike the impulse approximation the Vainshtein approximation does include to some extent the interaction between the electrons and the nucleus, by replacing the plane wave factor in (6-57) by a Coulomb wave function, but the impulse approximation appears to be more realistic in averaging the two-particle wave functions over the momentum distribution of the atom.

The transition matrix element in the impulse approximation can be reduced further by introducing the Fourier transform of the final state wave function $\varphi_n(r_2)$. We have

$$T_{n0} = \int d\mathbf{q} \int d\mathbf{p}\, \delta(\mathbf{q} + \mathbf{p} + \mathbf{k}' + \mathbf{k}) \widetilde{\varphi}_n^*(\mathbf{q}) \widetilde{\varphi}_0(\mathbf{p}) t\left(\tfrac{1}{2}(\mathbf{q} - \mathbf{k}'), \tfrac{1}{2}(\mathbf{p} - \mathbf{k})\right),$$

$$(6\text{-}58)$$

where $t(\boldsymbol{\alpha}, \boldsymbol{\beta})$ is the two-body (Coulomb) scattering amplitude for scattering from the state with momentum $\boldsymbol{\beta}$ to that with momentum $\boldsymbol{\alpha}$. In this form the impulse approximation can be seen to be close to various classical approximations that have received attention recently. In these methods, the classical two-body scattering cross section is employed, which is averaged over the velocity distributions of the bound electrons in various ways to obtain the cross section for the process of interest. The results suggest that these procedures may be reasonable if only order of magnitude cross sections are required. Details will not be given here, but the literature may be traced from the recent review by Burgess and Percival (1968).

6-5   EXCHANGE AND REARRANGEMENT COLLISIONS

By using wave functions having the correct symmetry there is no difficulty in including exchange effects in the close coupling and variational methods obtained earlier. There are however certain difficulties which arise when attempting to calculate the amplitude for a rearrangement or exchange collision with a perturbation scheme, such as the Born series.[6] For excitation processes not involving changes in the spin of the target, at higher energies, where the Born approximation may be expected to be valid, it is not necessary to make allowances for exchange scattering since the exchange amplitude decreases rapidly with increasing energy, but for reactions where the spin of the target changes, for instance in the reaction

$$e + He(1^1S) \rightarrow e + He(2^3S), \qquad (6-59)$$

which can only take place through electron exchange, it is necessary to develop an approximation equivalent to the Born approximation for direct scattering. As the difficulties encountered are common to all rearrangement collisions we shall consider the following model problem. Three distinct particles 1, 2 and 3, with masses M_1, M_2 and M_3 interact together

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[6] The same difficulties arise in theory of charge exchange which will be discussed in Chapter 8. See also the discussion in Chapter 4.

with potentials V_1, V_2 and V_3, where V_1 acts between particles 2 and 3, V_2 between 1 and 3, and V_3 between 1 and 2. We start by considering the rearrangement collision in which particle 1 is incident on a bound state of $(2 + 3)$, and in the final state particles 1 and 2 are bound and 3 is free.

$$1 + (2 + 3) \rightarrow 3 + (1 + 2). \tag{6-60}$$

We shall assume the total energy is below the threshold for the break-up of the system with three unbound particles. Coordinates will be introduced such that $\mathbf{R}_1$ is the relative position vector of 2 with respect to 3 and $\mathbf{r}_1$ is the position of 1 with respect to the center of mass of $(2 + 3)$. $(\mathbf{R}_2, \mathbf{r}_2)$ and $(\mathbf{R}_3, \mathbf{r}_3)$ can be defined similarly. The transition matrix element for reaction (6-60) is, following the general expressions obtained in Chapter 4,

$$T_{ji} = \int d\mathbf{R}_i \int d\mathbf{r}_i \, \Psi_0^{3*}(\mathbf{R}_3) e^{-i\mathbf{k}_j \cdot \mathbf{r}_3} (V_2 + V_3) \Psi_i^+(\mathbf{R}_1, \mathbf{r}_1). \tag{6-61}$$

The functions $\Psi_m^3(\mathbf{R}_3)$ form a complete set of orthonormal wave functions for the sub-system $(1 + 2)$ and in (6-61) it has been assumed that capture is into the ground state. In the incident channel the complete wave function Ψ^+ has the asymptotic form

$$\Psi^+ \xrightarrow[|\mathbf{r}_1| \to \infty]{} \Psi_0^1(\mathbf{R}_1) \left[e^{i\mathbf{k}_i \cdot \mathbf{r}_1} + f(\theta) \frac{e^{ik_i r_1}}{r_1} \right], \tag{6-62}$$

where the functions $\Psi_m^1(\mathbf{R}_1)$ are the complete set of eigenfunctions for the sub-system $(2 + 3)$. The center of mass momentum of particle 1 in the initial state is $\mathbf{k}_i \hbar$ and of particle 3 in the final state is $\mathbf{k}_j \hbar$ so that

$$\frac{\hbar^2}{2\mu_1} k_i^2 + \epsilon_0^1 = \frac{\hbar^2}{2\mu_3} k_j^2 + \epsilon_0^3, \tag{6-63}$$

where μ_i is the reduced mass of particle i with respect to the other two particles and $\epsilon_n^1, \epsilon_n^3$ are the binding energies of the m and nth state of sub-systems $(2 + 3)$ and $(1 + 2)$

respectively.

In the rearranged channel, the asymptotic form of Ψ is

$$\Psi_i^+ \xrightarrow[|r_3| \to \infty]{} g(\theta) \frac{e^{ik_j r_3}}{r_3} \Psi_o^3(\mathbf{R}_3),$$ (6-64)

where the rearranged amplitude is given by

$$g(\theta) = -\frac{\mu_3}{2\pi\hbar^2} T_{ji}(\theta),$$ (6-65)

and T_{ji} is given by equation (6-61). The Born approximation[7] for T_{ji} is obtained by substituting the incident unperturbed wave function for Ψ_i^+ in (6-61):—

$$T_{ji}^B = \int d\mathbf{R}_i \int d\mathbf{r}_i \, \Psi_o^{3*}(\mathbf{R}_3) e^{-i\mathbf{k}_j \cdot \mathbf{r}_3} (V_2 + V_3) e^{i\mathbf{k}_i \cdot \mathbf{r}_1} \Psi_o^1(\mathbf{R}_1).$$
(6-66)

This expression is defective for various reasons. Because the initial and final states of the system are not orthogonal, a constant added to the perturbation will contribute a finite amount to T_{ji}^B. This trouble does not occur in the Born approximation for excitation, because in that case the initial and final states are orthogonal. When particle 2 is infinitely heavy (as in electron scattering by hydrogen where 2 represents the proton), the cross section should vanish if the interaction between particles 1 and 3 is removed ($V_2 \to 0$). The matrix element T_{ji}^B does not have this property, but remains finite, again because of the non-orthogonality of the initial and final states. This difficulty does not occur in the Born approximation for direct excitation.

In practice these theoretical difficulties cannot be ignored, since the Born-Oppenheimer cross sections are often grossly in error, giving results greatly exceeding the measured

[7] In the particular case of electron exchange, this approximation is known as the Born-Oppenheimer approximation. See also Joachim and Mittleman (1965).

values. For example, the Born–Oppenheimer approximation provides cross sections about 20 times those observed at low energies for the $1^1S \rightarrow 2^3S$ excitation of helium.

To understand the origin of the difficulty let us examine the problem in the two-state approximation. For a trial wave function in the variational method we shall use the expression

$$\Psi_i^+ = \Psi_0^1(\mathbf{R}_1)F_0(\mathbf{r}_1) + \Psi_0^3(\mathbf{R}_3)G_0(\mathbf{r}_3). \tag{6-67}$$

With this choice the Euler equations obtained by varying the functional I, with respect to independent variations of F_0 and G_0, where

$$I = \int d\tau (\Psi^*(H - E)\Psi), \tag{6-68}$$

are

$$\int d\mathbf{R}_1 \Psi_0^{1*}(\mathbf{R}_1)(H - E)\left\{\Psi_0^1(\mathbf{R}_1)F_0(\mathbf{r}_1) + \Psi_0^3(\mathbf{R}_3)G_0(\mathbf{r}_3)\right\}$$

$$= 0, \tag{6-69a}$$

$$\int d\mathbf{R}_3 \Psi_0^{3*}(\mathbf{R}_3)(H - E)\left\{\Psi_0^1(\mathbf{R}_1)F_0(\mathbf{r}_1) + \Psi_0^3(\mathbf{R}_3)G_0(\mathbf{r}_3)\right\}$$

$$= 0. \tag{6-69b}$$

Using the Schrödinger equations for Ψ_0^1 and Ψ_0^3, these equations reduce to

$$\left(\nabla_{r_1}^2 + k_i^2 + U_{11}(r_1)\right)F_0(\mathbf{r}_1) = \frac{\mu_1}{\mu_3}\int d\mathbf{R}_1\left\{\Psi_0^{1*}(\mathbf{R}_1)\Psi_0^3(\mathbf{R}_3) \times\right.$$

$$\times \left. \left[-\nabla_{r_3}^2 - k_j^2 + \frac{2\mu_3}{\hbar^2}(V_1 + V_2)\right]G_0(\mathbf{r}_3)\right\}, \tag{6-70a}$$

$$\left(\nabla_{r_3}^2 + k_j^2 + U_{33}(\mathbf{r}_3)\right)G_0(\mathbf{r}_3) = \frac{\mu_3}{\mu_1}\int dR_3\left\{\Psi_0^{3*}(\mathbf{R}_3)\Psi_0^1(\mathbf{R}_1) \times\right.$$

$$\times \left. \left[-\nabla_{r_1}^2 - k_i^2 + \frac{2\mu_1}{\hbar^2}(V_3 + V_2)\right]F_0(\mathbf{r}_1)\right\}, \tag{6-70b}$$

where U_{11}, U_{33} are the static interactions in the initial and final states.

$$U_{11}(r_1) = -\frac{2\mu_1}{\hbar^2} \int d\mathbf{R}_1 \left\{ \Psi_0^{1*}(\mathbf{R}_1)\Psi_0^1(\mathbf{R}_1)(V_2 + V_3) \right\}, \quad (6\text{-}71a)$$

$$U_{33}(r_3) = -\frac{2\mu_3}{\hbar^2} \int d\mathbf{R}_3 \left\{ \Psi_0^{3*}(\mathbf{R}_3)\Psi_0^3(\mathbf{R}_3)(V_1 + V_2) \right\}. \quad (6\text{-}71b)$$

The boundary conditions to be satisfied by F_0 and G_0 are

$$F_0(\mathbf{r}_1) \sim e^{i\mathbf{k}_i \cdot \mathbf{r}_1} + r_1^{-1} \exp{(ik_ir_1)}f(\theta_1), \quad (6\text{-}72)$$

$$G_0(\mathbf{r}_3) \sim r_3^{-1} \exp{(ik_jr_3)}g(\theta_3).$$

The plane wave, or 'Born–Oppenheimer' approximation, then consists in replacing $F_0(\mathbf{r}_1)$ by $\exp{(i\mathbf{k}_i \cdot \mathbf{r}_1)}$ in (6-70b) and omitting U_{33}. In this approximation the terms $-(\nabla_{r_1}^2 + k_i^2)F_0(\mathbf{r}_1)$ occurring on the right hand side of (6-70) vanish, but as pointed out by Feenberg (1933) these terms should be of first order in the potential since from equation (6-70a), to first order,

$$\cdot\left(\nabla_{r_1}^2 + k_i^2\right) F_0(\mathbf{r}_1) \simeq - U_{11}(r_1)F_0(\mathbf{r}_1). \quad (6\text{-}73)$$

This suggests that a more consistent first order approximation would be obtained by replacing the operator $\left(\nabla_{r_1}^2 + k_i^2\right)$ in (6-70b) by $(-U_{11}(r_1))$ and at this stage making a plane wave approximation. We then find

$$T_{ji}^E = \int d\mathbf{R}_i \int d\mathbf{r}_i \, \Psi_0^{3*}(\mathbf{R}_3)e^{-\mathbf{k}_j \cdot \mathbf{r}_3}\left[\frac{\hbar^2}{2\mu_1} U_{11}(r_1) + \right.$$

$$\left. + (V_2 + V_3)\, e^{i\mathbf{k}_i \cdot \mathbf{r}_1} \Psi_0^1(\mathbf{R}_1) \right]. \quad (6\text{-}74)$$

This has been termed the first order exchange approximation[8] by Bell and Moiseiwitsch (1963). The matrix element T_{ji}^E suffers from neither of the defects mentioned earlier and numerical calculation shows that the results obtained are much

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[8] A variety of first order approximations have been studied by Mittleman (1962). See also Joachim and Mittleman (1965).

closer to those found by integrating the coupled equations
(6-70a,b) than those of the Born-Oppenheimer method. The
static interaction U_{11} occurring in (6-74) may be thought of as
correcting for the lack of orthogonality of the initial and final
wave functions and indeed if the initial and final wave functions
are orthogonalized before applying the first order perturbation
theory the same expression may be obtained.

The distorted wave method

An improved approximation to the coupled equations
(6-70a,b) is the distorted wave approximation which reads

$$T_{ji}^{DW} = \int d\mathbf{R}_i \int d\mathbf{r}_i \Psi_0^{3*}(\mathbf{R}_3)\mathcal{G}(\mathbf{r}_3)\left[-\frac{h^2}{2\mu_1}\left(\nabla_{r_1}^2 + k_i^2\right) + \right.$$

$$\left. + (V_2 + V_3)\right]\Psi_0^1(\mathbf{R}_1)\mathfrak{F}(\mathbf{r}_1), \qquad (6-75)$$

where $\mathcal{G}$ and $\mathfrak{F}$ satisfy the uncoupled equations

$$\left(\nabla_{r_1}^2 + k_i^2 + U_{11}\right)\mathfrak{F}(\mathbf{r}_1) = 0, \qquad (6-76a)$$

$$\left(\nabla_{r_3}^2 + k_j^2 + U_{33}\right)\mathcal{G}(\mathbf{r}_3) = 0, \qquad (6-76b)$$

with the boundary conditions

$$\mathfrak{F}(\mathbf{r}_1) \sim e^{i\mathbf{k}_i \cdot \mathbf{r}_1} + r_1^{-1}\exp(ik_ir_1)\bar{f}(\theta_1,\varphi_1), \qquad (6-77a)$$

$$\mathcal{G}(\mathbf{r}_3) \sim e^{-i\mathbf{k}_j \cdot \mathbf{r}_3} + r_3^{-1}\exp(ik_jr_3)\bar{g}(\theta_3,\varphi_3). \qquad (6-77b)$$

From the equation satisfied by $\mathfrak{F}$ we have, automatically,
that $\left(\nabla_{r_1}^2 + k_i^2\right)\mathfrak{F}$ is equal to $U_{11}\mathfrak{F}$,, so that none of the
difficulties of the Born-Oppenheimer approximation occur in
the distorted wave approximation. The cross sections provided
by the distorted wave approximation for the $1^1S \rightarrow 2^3S$ excitation of
helium (Massey and Moiseiwitsch (1954) are compared with the
experimental measurements in figure 6-7. Although better than
the Born-Oppenheimer approximation, the agreement is still not
satisfactory.
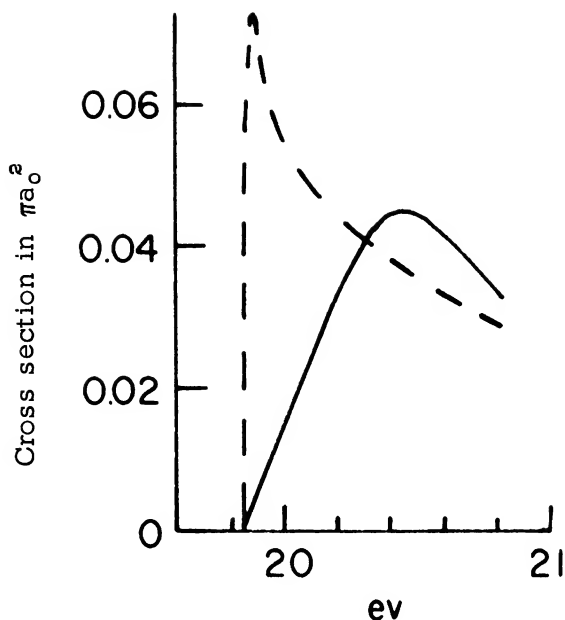
Figure 6-7.   Low energy cross section for excitation of the 2^3S state of helium from the ground state by electron impact.

     ————   Experimental curve (Schulz and Fox, 1957).

     - - - - -   Exchange distorted wave method (Massey and Moiseiwitsch, 1954).

The Ochkur approximation

A different approach to obtaining an adequate high energy approximation for exchange scattering is due to Ochkur (1964). The Born-Oppenheimer transition matrix element can be expanded in inverse powers of k_i^2 and at high energies only the lowest term in the expansion will be significant. As the Born-Oppenheimer approximation is only expected to be accurate at high energies, only the lowest term in the expansion need be correct and the higher terms may be in error. However, it is these terms that dominate the amplitude if an attempt is made to use the Born-Oppenheimer approximation at low energies. The suggestion of Ochkur is to isolate the lowest term in the expansion and to use this term at all energies.

Let us consider the particular case of the exchange scattering amplitude in electron-hydrogen scattering. Then the exchange amplitude for excitation to the nth level of hydrogen is

$$g_{no}(\theta,\varphi) = -\frac{1}{2\pi}\int\varphi_n^*(\mathbf{r}_2)e^{-i\mathbf{k}_n\cdot\mathbf{r}_1}\left(\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\right.$$

$$\left.-\frac{1}{r_2}\right)\varphi_0(\mathbf{r}_1)e^{i\mathbf{k}_0\cdot\mathbf{r}_2}d\mathbf{r}_1 d\mathbf{r}_2, \qquad (6\text{-}78)$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the position vectors of the two electrons. The term $(1/r_2)$, which represents the interaction between electron 2 and the proton, does not contribute to the terms of lowest order in $(1/k_0^2)$ and may be dropped. The integral over $\mathbf{r}_2$ is then of the form

$$I(\mathbf{r}_1) = \int d\mathbf{r}_2\varphi_n^*(\mathbf{r}_2)\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}e^{i\mathbf{k}_0\cdot\mathbf{r}_2}. \qquad (6\text{-}79)$$

Introducing the Fourier transform of $\varphi_n(\mathbf{r}_2)$ by

$$\widetilde{\varphi}_n(\mathbf{p}) = \left(\frac{1}{2\pi}\right)^{3/2}\int e^{-i\mathbf{p}\cdot\mathbf{r}_2}\varphi_n(\mathbf{r}_2)d\mathbf{r}_2,$$

we find that

$$I(\mathbf{r}_1) = \int d\mathbf{p}\int d\mathbf{r}_2\left(\frac{1}{2\pi}\right)^{3/2}\widetilde{\varphi}_n^*(\mathbf{p})\frac{e^{i(\mathbf{p}+\mathbf{k}_o)\cdot\mathbf{r}_2}}{|\mathbf{r}_1-\mathbf{r}_2|} \qquad (6\text{-}80)$$

$$= \sqrt{\frac{2}{\pi}}\int d\mathbf{p}\,\widetilde{\varphi}_n^*(\mathbf{p})\frac{e^{+i(\mathbf{p}+\mathbf{k}_0)\cdot\mathbf{r}_1}}{|\mathbf{p}+\mathbf{k}_0|^2}, \qquad (6\text{-}81)$$

where we have used the result that

$$\int\frac{e^{i\mathbf{k}\cdot\mathbf{x}}}{|\mathbf{x}-\mathbf{y}|}d\mathbf{x} = \frac{4\pi}{k^2}e^{i\mathbf{k}\cdot\mathbf{y}}.$$

For large k_0^2, $|\mathbf{p}+\mathbf{k}_0|^2$ in the denominator of (6-81) can be replaced by k_0^2 and the integral then reduces to the Fourier transform of $\widetilde{\varphi}_n(\mathbf{p})$, which is of course just $\varphi_n(\mathbf{r}_1)$.

$$I(\mathbf{r}_1) \xrightarrow[\text{large } k_0^2]{} \frac{(4\pi)}{k_0^2} e^{i\mathbf{k}_0 \cdot \mathbf{r}_1} \varphi_n^*(\mathbf{r}_1), \qquad (6\text{-}82)$$

The exchange amplitude with this approximation for $I(\mathbf{r}_1)$ is

$$g_{no}(\theta) = \frac{-2}{k_0^2} \int \varphi_n^*(\mathbf{r}_1) e^{i\mathbf{k}_0 \cdot \mathbf{r}_1} \varphi_0(\mathbf{r}_1) e^{-i\mathbf{k}_n \cdot \mathbf{r}_1} d\mathbf{r}_1 \qquad (6\text{-}83)$$

Referring to equation (6-23), the integral is seen to be proportional to the direct Born approximation amplitude $f_{no}(\theta)$, and in fact,

$$g_{no}(\theta) = \frac{K^2}{k_0^2} f_{no}(\theta), \qquad (6\text{-}84)$$

where $\mathbf{K} = \mathbf{k}_0 - \mathbf{k}_n$. The differential cross section for e – H excitation for a beam of unpolarized electrons is then

$$\frac{d\sigma}{d\Omega} = \frac{k_n}{4k_0} \left[|f_{no}(\theta)|^2 \left\{ \left(1 + \frac{K^2}{k_0^2}\right)^2 + 3\left(1 - \frac{k^2}{k_0^2}\right)^2 \right\} \right].$$

$$(6\text{-}85)$$

The total cross section for exchange scattering behaves like $1/k_0^6$ at high energies in contrast to the direct cross section which is proportional to $1/k_0^2$.

As presented here the Ochkur approximation is not concerned with a variational principle, but Rudge (1965) has shown that if the trial functions

$$\Phi_i = e^{i\mathbf{k}_0 \cdot \mathbf{r}_2} \varphi_0(\mathbf{r}_1),$$

$$\Phi_j = -\frac{\varphi_n^*(\mathbf{r}_2)}{\varphi_0(\mathbf{r}_1)(k_n - i)^2} \nabla_1^2 \left[\varphi_0(\mathbf{r}_1) \exp(-i\mathbf{k}_n \cdot \mathbf{r}_1) \right] \qquad (6\text{-}86)$$

are used for the initial and final states, an equivalent variational approximation is obtained. These trial functions have the property of being orthogonal and asymptotically go over to the usual plane wave approximation.

Ochkur and Bratsev (1965) have discussed the excitation of triplet states in helium using the Ochkur approximation and Morrison and Rudge (1966) have employed Rudge's

modification of Ochkur's approximation. Some results for the excitation of the ^{3}S state are shown in figure 6-8. It is seen that no particularly close agreement is obtained with the experimental results for these reactions. However, for ionization, as we shall see in the next section, the Ochkur approximation provides cross sections which are in reasonable accord with the experiments.
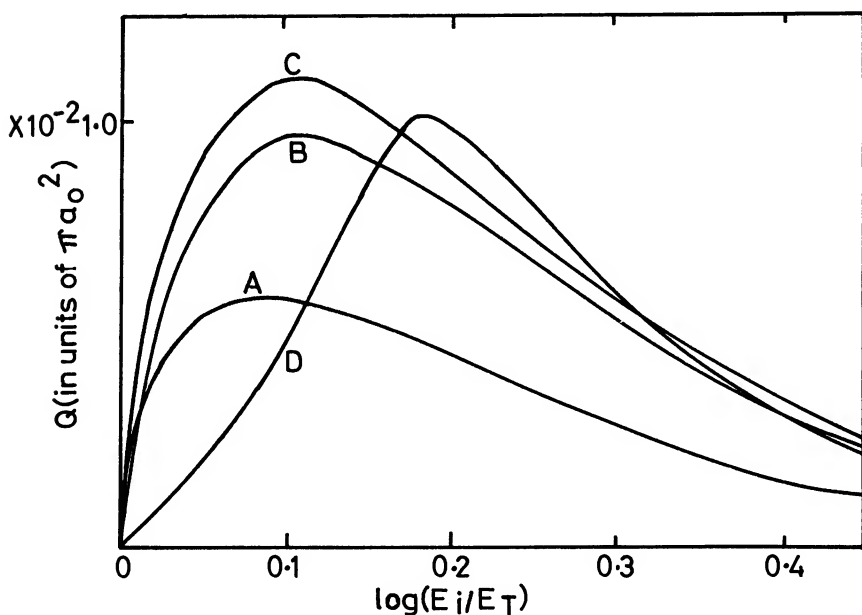
Figure 6-8.   The 1^1S → 3^3S excitation of helium by electron impact.

    (A)   Modified Ochkur approximation (Morrison and Rudge, 1967).

    (B),(C) Ochkur approximation with different helium wave functions (Ochkur and Bratsev, 1965).

    (D)   Experimental data (St. John et al., 1964).

E_i is the incident and E_T the threshold energy.

6-6   IONIZATION

When the total energy of the system is great enough the target atom may be ionized in an electron-atom collision; that is, one or several electrons may be ejected. As an example, the ionization of hydrogen by electron impact will be discussed, but the approximations employed may be extended to more complicated systems.

The total wave function[9] $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ can always be expanded in terms of the complete set of hydrogenic wave functions $\varphi_n(\mathbf{r})$, as in equation (5-43). Assuming that in the incident state electron 1 is free and 2 is bound, and displaying the continuum terms explicitly, the expansion is (in the unsymmetrized form)

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_n \left\{ \varphi_n(\mathbf{r}_2)F_n(\mathbf{r}_1) + \varphi_n(\mathbf{r}_1)G_n(\mathbf{r}_2) \right\} +$$

$$+ \int d\mathbf{K} \left\{ \varphi_\mathbf{K}(\mathbf{r}_2)F_\mathbf{K}(\mathbf{r}_1) + \varphi_\mathbf{K}(\mathbf{r}_1)G_\mathbf{K}(\mathbf{r}_2) \right\}. \quad (6\text{-}87)$$

Here the sum over n runs over the bound hydrogenic states and the integral over $\mathbf{K}$ is over the continuum states $\varphi_\mathbf{K}$, where $\mathbf{K}$ is the momentum of the state, with energy $K^2/2$. The normalization assumed for the continuum states is

$$\int d\mathbf{r} \varphi_\mathbf{K}^*(\mathbf{r})\varphi_{\mathbf{K}'}(\mathbf{r})d\mathbf{r} = \delta(\mathbf{K} - \mathbf{K}'). \quad (6\text{-}88)$$

The normalization condition does not completely define the functions $\varphi_\mathbf{K}(\mathbf{r})$, because we must decide on the boundary conditions that we require $\varphi_\mathbf{K}$ to satisfy. For example, we can use either the functions $\varphi_\mathbf{K}^+$, with outgoing wave boundary conditions or the functions $\varphi_\mathbf{K}^-$ with ingoing waves. A particular choice will be made later.

As explained in Chapter 5, the functions $F_\mathbf{K}$ and $G_\mathbf{K}$ can be chosen to be non-singular in K and this insures that only the functions F_n contribute in the asymptotic region to

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[9] The notation established for electron-hydrogen collisions in Chapter 5, and earlier in this chapter, will be followed here, using atomic units.

direct scattering and only the functions G_n contribute in the asymptotic region for rearrangement scattering. In ionization where both electrons appear in the final state, there can be no distinction between the direct and rearranged situations, but it is useful to speak of direct scattering if electron 2 is ejected with a smaller energy than the final energy of electron 1 and of exchange scattering if the reverse situation applies.

The boundary conditions satisfied by F_n and G_n are those discussed earlier:

$$F_0(\mathbf{r}_1) \sim e^{i\mathbf{k}_0 \cdot \mathbf{r}_1} + r_1^{-1} e^{ik_0 r_1} f_0(\theta_1),$$

$$F_n(\mathbf{r}_1) \sim r_1^{-1} e^{ik_n r_1} f_n(\theta_1), \quad n \neq 0, \tag{6-89}$$

$$G_n(\mathbf{r}_2) \sim r_2^{-1} e^{ik_n r_2} g_n(\theta_2) \quad \text{all } n,$$

while for $F_{\mathbf{K}}(\mathbf{r}_1)$ and $G_{\mathbf{K}}(\mathbf{r}_2)$ we must have that [10]

$$F_{\mathbf{K}}(\mathbf{r}_1) \sim r_1^{-1} e^{i(kr_1 + a(r_1))} f(\mathbf{K}, \mathbf{k}), \quad K^2 < k^2,$$

$$G_{\mathbf{K}}(\mathbf{r}_2) \sim r_2^{-1} e^{i(kr_2 + a(r_2))} g(\mathbf{K}, \mathbf{k}), \quad K^2 < k^2,$$

$$r_1 F_{\mathbf{K}}(\mathbf{r}_1) \xrightarrow[r_1 \to \infty]{} 0, \quad K^2 > k^2 \tag{6-90}$$

$$r_2 G_{\mathbf{K}}(\mathbf{r}_2) \xrightarrow[r_2 \to \infty]{} 0, \quad K^2 > k^2.$$

The restriction that $F_{\mathbf{K}}$ and $G_{\mathbf{K}}$ must vanish at large distances when $K^2 > k^2$, is to ensure that each direct and exchange amplitude is counted only once. By conservation of energy, K^2 and k^2 are related by

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[10] The following conditions apply when $|\mathbf{r}_1 - \mathbf{r}_2|$, r_1 and r_2 are all large. If $|\mathbf{r}_1 - \mathbf{r}_2|$ is small, there are difficulties in specifying the boundary conditions when the interaction is of long range (Nuttall, 1967).

$$E = \frac{1}{2} k_0^2 + \epsilon_0 = \frac{1}{2} k_n^2 + \epsilon_n = \frac{1}{2} (k^2 + K^2). \tag{6-91}$$

The appearance of phase factors $a(r)$ in the asymptotic forms of F_K and G_K is a consequence of the long range nature of the interactions. For discrete transitions the target electron completely shields the scattered electron from the nuclear charge if the target is a neutral atom, and the scattered electron can be described by ordinary plane or spherical waves at large distances. In ionization, the screening is not complete and the phase factors a are of the logarithmic type that were encountered in the treatment of Coulomb scattering in Chapter 3.

The total ionization cross section for distinguishable electrons would be

$$\sigma(\text{ion}) = \int_{K^2 < k^2} d\mathbf{K} \; \frac{k}{k_0} \int d\Omega(\hat{\mathbf{k}}) [|f(\mathbf{K}, \mathbf{k})|^2 + |g(\mathbf{K}, \mathbf{k})|^2] \tag{6-92}$$

where the integration over $\mathbf{K}$ is carried out only for $K^2 < k^2$, to avoid double counting. The sum over final states is consistent with the normalization and closure relations assumed for the hydrogenic wave functions. For indistinguishable electrons, amplitudes of a definite spin s are formed as in equation (5-44) and the cross section for an unpolarized beam is (compare equation 5-45)

$$\sigma(\text{ion}) = \int_{K^2 < k^2} d\mathbf{K} \; \frac{k}{k_0} \int d\Omega(\hat{\mathbf{k}}) \{ |f(\mathbf{K}, \mathbf{k})|^2 + |g(\mathbf{K}, \mathbf{k})|^2 -$$

$$- \text{Re}[f(\mathbf{K}, \mathbf{k}) g^*(\mathbf{K}, \mathbf{k})] \}. \tag{6-93}$$

Instead of restricting the domain in which $f(\mathbf{K}, \mathbf{k})$ is defined to the region $K^2 < k^2$, and remembering that there is no real distinction between direct and exchange ionization, we can define $f(\mathbf{K}, \mathbf{k})$ for $K^2 > k^2$ by

$$f(\mathbf{K}, \mathbf{k}) \equiv g(\mathbf{k}, \mathbf{K}), \quad K^2 > k^2. \tag{6-94}$$

An alternative form for (6-93) is, where the integration is now over all allowed values of K^2:—

$$\sigma(\text{ion}) = \int d\mathbf{K} \frac{k}{k_0} \int d\Omega(\hat{\mathbf{k}}) \left[|f(\mathbf{K}, \mathbf{k})|^2 - \right.$$

$$\left. - \frac{1}{2} \operatorname{Re}\{f(\mathbf{K}, \mathbf{k})f^*(\mathbf{k}, \mathbf{K})\} \right]. \qquad (6\text{-}95)$$

Calculation of $f(\mathbf{K}, \mathbf{k})$

In calculating $f(\mathbf{K}, \mathbf{k})$ let us first treat the case in which the interaction is of short range. It is then possible to proceed as in Chapter 4 and it is found that

$$-2\pi f(\mathbf{K}, \mathbf{k}) = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \left[(H - E)\Phi_\beta(\mathbf{r}_1, \mathbf{r}_2)\right]^* \psi_\alpha^+(\mathbf{r}_1, \mathbf{r}_2),$$

$$(6\text{-}96)$$

where Φ_β is the wave function of the final unperturbed state.[11] Several choices may be made for Φ_β. For example, if none of the interaction is included in specifying the final state, then

$$\Phi_\beta = (2\pi)^{-3/2} \exp\left[i\mathbf{K} \cdot \mathbf{r}_2 + i\mathbf{k} \cdot \mathbf{r}_1\right]. \qquad (6\text{-}97)$$

In this form, the lack of distinction between direct and exchange scattering is particularly obvious. Equally it is possible to include the interaction between electron 2 and the proton $(1/r_2)$ in defining Φ_β, so that

$$\Phi_\beta = (2\pi)^{-3/2} \varphi_{\mathbf{K}}^-(\mathbf{r}_2) \exp(i\mathbf{k} \cdot \mathbf{r}_1). \qquad (6\text{-}98)$$

The value of the matrix element obtained with either choice of Φ_β is, of course, the same. It is important to notice in defining Φ_β, we must use $\varphi_{\mathbf{K}}^-$ rather than $\varphi_{\mathbf{K}}^+$. The reasons for

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[11] The matrix element could have been written $(\Phi_\beta, V_\beta \psi_\alpha^+)$, where V_β is the perturbation in the final state. As $V_\beta \Phi_\beta = (H - E)\Phi_\beta$, it is equally possible to use $((H - E)\Phi_\beta, \psi_\alpha^+)$, which allows us to consider differing forms of Φ_β without changing the perturbation in the matrix element.

this were explained in Chapters 3 and 4 in connection with the problem of scattering from two potentials and the distorted wave approximation.

The general problem of defining amplitudes and cross sections where several particles appear in final or initial states has been discussed fully by Gerjuoy (1958) and also by Delves (1958). The amplitude (6-94) with the Φ_β given by (6-95) can be obtained by examining the asymptotic form of Ψ^+ starting from the integral equation

$$\Psi_\alpha^+ = \Phi_\alpha + G_0^+ V \Psi_\alpha^+, \tag{6-99}$$

where V is the full interaction and G_0^+ is Green's function for 3 non-interacting particles. The Green's functions for N non-interacting particles have been given by Sommerfeld (1964) and in the present case (treating the interactions as if short range),

$$G_0(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1', \mathbf{r}_2') = \frac{i}{4} \left(\frac{\lambda}{4\pi^2}\right)^{5/2} \frac{H_{5/2}^1 \{\sqrt{\lambda} \,|\boldsymbol{\rho} - \boldsymbol{\rho}'|\}}{|\boldsymbol{\rho} - \boldsymbol{\rho}'|^{5/2}}$$

$$\tag{6-100}$$

where $H_\alpha^1 = J_\alpha + iN_\alpha$, $\boldsymbol{\rho}$ is a 6-dimensional vector with components $(\mathbf{r}_1, \mathbf{r}_2)$, and $\lambda = 2E$. To establish the asymptotic form of (6-100) and hence of (6-99) the value of the Green's function is required for $\mathbf{r}_1, \mathbf{r}_2$ large, that is, for $|\boldsymbol{\rho}|$ large. The orientation of $\boldsymbol{\rho}$ is determined by the following considerations. In an experiment, if an ionization is detected by collecting an electron simultaneously in each of two counters situated at distances $\mathbf{r}_1$ and $\mathbf{r}_2$ from the scattering center, then the time of flight t of each electron must be the same. If v_1 and v_2 are the velocities of the electrons,

$$t = \frac{r_1}{v_1} = \frac{r_2}{v_2} \tag{6-101}$$

and in atomic units, $v_1 = k$, $v_2 = K$. The asymptotic form of G_0 for large $\boldsymbol{\rho}$, satisfying this condition, is

$$G_0 \sim \frac{e^{-(3i\pi/4)}}{2\sqrt{\lambda}} \left(\frac{\sqrt{\lambda}}{2\pi\rho}\right)^{5/2} e^{i\sqrt{\lambda}\rho} \exp\left[-i\mathbf{k}\cdot\mathbf{r}_1' - i\mathbf{K}\cdot\mathbf{r}_2'\right]$$

$$\tag{6-102}$$

From (6-99) and (6-102) it is easy to verify that the scattering amplitude is given by (6-96) with Φ_β given by (6-97).

Coulomb interactions

The corresponding amplitude for Coulomb interactions has been obtained by Peterkop (1962) and Rudge and Seaton (1965), by examining the asymptotic form of the equation

$$\left(\nabla_1^2 + \nabla_2^2 + \frac{2}{r_1} + \frac{2}{r_2} - \frac{2}{|r_1 - r_2|} - 2E \right) \Psi = 0. \quad (6-103)$$

As before, the region of configuration space of interest is that for which $\rho = \sqrt{r_1^2 + r_2^2}$ is large and for which

$$t = \frac{r_1}{k} = \frac{r_2}{K}. \quad (6-104)$$

From (6-104), the Schrödinger equation (6-103) in the asymptotic region can be written as

$$\left(\nabla_1^2 + \nabla_2^2 + \frac{Z}{\rho} - \lambda \right) \Psi = 0, \quad (6-105)$$

where Z is an effective charge and, as before, $\lambda = 2E$. Equating the potential energies in equations (6-103) and (6-105),

$$\frac{Z}{\rho} = \frac{2}{r_1} + \frac{2}{r_2} - \frac{2}{|r_1 - r_2|}, \quad (6-106)$$

setting $t = \frac{\rho}{\sqrt{\lambda}}$, we have

$$\frac{Z}{\sqrt{\lambda}} = \left(\frac{2}{k} + \frac{2}{K} - \frac{2}{|k - K'|} \right). \quad (6-107)$$

Then (Peterkop, 1960) the asymptotic solution of (6-105) is $(E \neq 0)$

$$\Psi \sim \rho^{-5/2} e^{i\sqrt{\lambda}\rho} e^{i\left(\frac{Z}{\sqrt{\lambda}} \log \rho\right)} a, \quad (6-108)$$

where a is independent of ρ. Comparing with (6-102), an extra phase factor due to the effective interaction (Z/ρ) appears, and comparison with expressions of the form (6-90) enables the phase $a(r)$ to be chosen, although not uniquely.

The scattering amplitude $f(\mathbf{K},\mathbf{k})$ will still be given (apart from a phase factor independent of ρ) by (6-94) providing a suitable choice of final state functions Φ_β can be made. To take into account the imperfect screening, each electron can be considered to move in a Coulomb field, electron 1 in a field due to an effective charge Z_1 situated at the origin and electron 2 in a field of effective charge Z_2. Then

$$\Phi_\beta = (2\pi)^{3/2}\varphi_{\mathbf{K}}^-(Z_2,\mathbf{r}_2)\varphi_{\mathbf{k}}^-(Z_1,\mathbf{r}_1). \tag{6-109}$$

The functions $\varphi_{\mathbf{K}}^-$ are given by $\varphi_{\mathbf{K}} = (2\pi)^{-3/2}\psi^{c^-}$ where ψ^{c^-} is defined by equation (3-63), taking $a = -2Z$. The asymptotic form of $\varphi_{\mathbf{K}}^-(Z,\mathbf{r})$ is

$$\varphi_{\mathbf{K}}^-(Z,\mathbf{r}) \sim (2\pi)^{-3/2}\left[e^{i[\mathbf{K}\cdot\mathbf{r} - Z/K\log\{Kr(1-\cos\theta)\}]} + \right.$$

$$\left. + f_c^-(\theta)r^{-1}\, e^{-[Kr + Z/K\log 2Kr]}\right]. \tag{6-110}$$

The charges Z_1 and Z_2 must be chosen so that the potential energy of the system in the asymptotic region is given correctly. This requires

$$\frac{Z}{\rho} = \frac{Z_1}{r_1} + \frac{Z_2}{r_2}, \tag{6-111}$$

from which

$$\frac{Z_1}{k} + \frac{Z_2}{K} = \frac{2}{K} + \frac{2}{k} - \frac{2}{|\mathbf{K} - \mathbf{k}|}. \tag{6-112}$$

One of Z_1 and Z_2 can be chosen at will but the other is determined by this relation. The scattering amplitude is then

$$-2\pi f(\mathbf{K},\mathbf{k}) = e^{i\beta(\mathbf{K},\mathbf{k})}(2\pi)^{-3/2}\int\left\{[H - E]\,\varphi_{\mathbf{K}}^-(Z_1,\mathbf{r}_1)\varphi_{\mathbf{k}}^-(Z_2,\mathbf{r}_2)\right\}^*$$

$$\Psi_a^+(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2, \tag{6-113}$$

where the phase β may be shown to be (Rudge and Seaton, 1965)

$$\beta(\mathbf{K},\mathbf{k}) = \frac{2Z_1}{k}\log\left(\frac{K}{\lambda}\right) + \frac{2Z_2}{K}\log\left(\frac{K}{\lambda}\right). \tag{6-114}$$

Threshold behavior

From the general form of the scattering amplitude
(6-113), Rudge and Seaton (1965) have shown that the ionization
cross section should vary linearly with energy at threshold.[12]
Recently, some measurements of the ionization of hydrogen very
close to threshold have been made by McGowen et al. (1968).
These results suggest that within 0.4 ev of the threshold, the
cross section behaves non-linearly with energy but above 0.4
ev there is a linear region. Measurements so close to thresh-
old are very difficult and it would probably be unwise to include
anything very definite from these results, which, however are
of great interest.

Approximations

A variety of approximate calculations have been carried
out on the basis of the amplitude (6-113) but in none of them
has the correct relationship between Z_1 and Z_2 been retained.
In the most simple approximation, the Born approximation, the
complete wave function Ψ which appears in (6-113) is replaced by
the unperturbed wave

$$\Psi^+(\mathbf{r}_1, \mathbf{r}_2) \simeq \varphi_0(\mathbf{r}_2) e^{i\mathbf{k}_0 \cdot \mathbf{r}_1} \qquad (6-115)$$

and at the same time it is usual to set $\beta = 0$ and take $Z_1 = 0$,
$Z_2 = 1$, so that the ejected electron screens the scattered
electron completely. In this approximation interference bet-
ween the direct and exchange amplitudes is neglected and the
second term in (6-95) is ignored.

Exchange effects are included in the Born-Oppenheimer
approximation. Here β is again taken to be zero, but when
$k > K$, the scattered electron is screened ($Z_1 = 0$, $Z_2 = 1$), but
for $k < K$, the ejected electron is screened ($Z_1 = 1$, $Z_2 = 0$)
and the complete expression (6-95) is employed.

These plane wave approximations agree well with ex-
periment at energies above 200 ev in the case of $e^- - H$, and
400 ev for $e^- - He$ collisions; but at low energies the calcu-
lated cross sections are much too large. Some improvement
can be obtained with other choices of Z_1 and Z_2.

At lower energies, a more promising approximation is
that introduced by Ochkur and discussed above for excitation.
In this approximation, the cross section becomes (Ochkur, 1964)

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[12] This conclusion has been challenged by Temkin (1966).

$$\sigma(\text{ion}) = \int\limits_{K^2 < k^2} d\mathbf{K} \int d\Omega(\hat{\mathbf{k}}) \frac{k}{2k_0} |f(\mathbf{K}, \mathbf{k})|^2 \left(1 - \frac{|\mathbf{K} - \mathbf{k}_0|^2}{k_0^2} + \right.$$

$$\left. + \frac{|\mathbf{K} - \mathbf{k}_0|^4}{k_0^4}\right). \qquad\qquad (6\text{-}116)$$

The calculations of Peach (1966) for ionization of hydrogen and helium are shown in figure 6-9 for the Ochkur approximation and for modifications of the Born approximations. The Ochkur approximation is seen to be quite successful.

Calculations for the ionization of several different atoms have been carried out in the Born approximation and also in the approximation of Ochkur. We may single out the work of Peach (1965, 1966a,b) on H, He, Li, Be, Na, Mg, and that of Bates et al. (1965) on Na, from which the literature may be traced. Few attempts have been made to improve on the use of the unperturbed function of the initial state, but a step in this direction has been taken by Burke and Taylor (1965), who used a close coupling wave function in the 1s - 2s - 2p approxima- tion for Ψ^+ and found that the effects of departure from a plane wave were considerable.

Note added in proof (see page 247)

        In the last year, absolute measurements of differential cross sections for elastic and inelastic scattering of electrons by atoms have become available in the energy range 50 to 500 ev (J. P. Bromberg, 1969. J. chem. Phys., **50**, 3906; G. E. Chamberlain, S. R. Mielczavek and C. E. Kuyatt, Abstract submitted to XIth International Conference on the Physics of Electronic and Atomic Collisions, Cambridge, Mass., 1969.) The general conclusions stated on pages 247 and 248, above, are unaltered. In the case of elastic scattering of electrons by helium, calculations based on the polarised orbital method (R. W. La Bahn and J. Callaway, 1969, Phys. Rev., **180**, 91) reproduce the experimental cross sections down to angles of a few degrees.
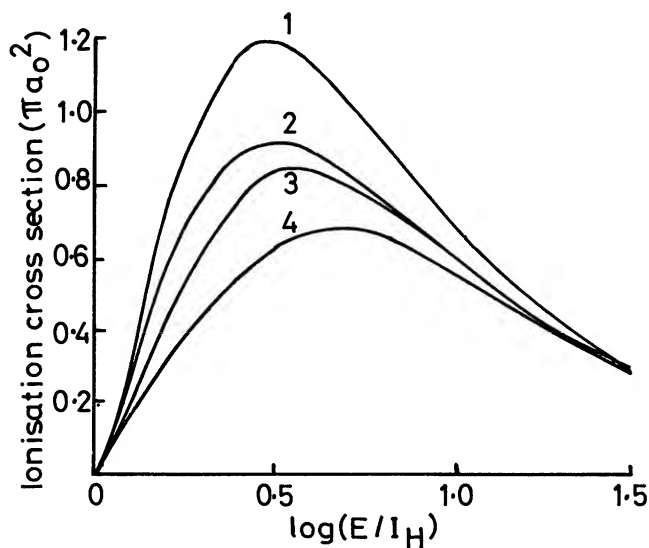
(a) Hydrogen
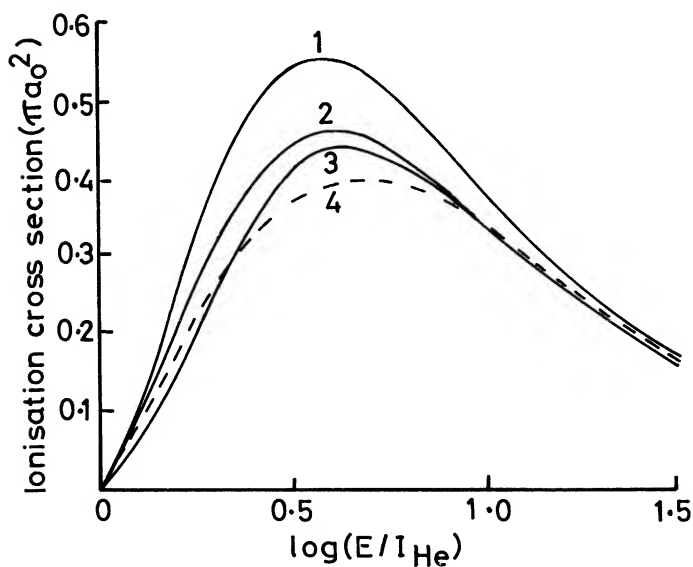
(b) Helium

Figure 6-9a,b.   Cross sections for the ionization of hydrogen and helium by electron impact (after Peach, 1966).

    1.   Calculated cross sections, Born approximation.
    2.   Calculated cross section, Born-exchange approximation.
    3.   Calculated cross section, Ochkur's approximation.
    4.   Experimental cross section. (H: Fite and Brackman, 1958;
            He: Schram et al., 1965).

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Chapter 7

AUTO-IONIZATION AND RESONANCES
IN ELECTRON-ATOM COLLISIONS

7-1 THE FORMATION AND PRODUCTION OF RESONANT STATES

In earlier chapters, we have seen that metastable states, with life times long compared with natural collision times, may be formed in a scattering process, and that the existence of such states leads to resonant behavior in cross sections as a function of energy. In general there are two kinds of experiments which demonstrate the existence of a resonant state.[1] There are "formation" experiments in which the scattered particles combine with the target to form a metastable complex:

$$A + B \to C^*. \tag{7-1}$$
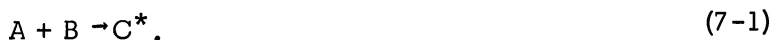
Subsequently the metastable state C^* may decay into the incident channel

$$C^* \to A + B, \tag{7-2}$$

or, if sufficient energy is available, other decays may be possible. For example C^* may decay into excited states of A and B,

$$C^* \to A^* + B^*. \tag{7-3}$$

Some examples of this kind of experiment have been noted in connection with electron scattering by atoms in earlier

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[1] Resonant states in electron-atom collisions have been the subject of two excellent recent reviews: Burke (1966, 1968); Smith (1966). Very complete bibliographies may be found in these works.

chapters. We saw that below the first $(n = 2)$ excitation threshold several resonances occur in electron-hydrogen atom scattering:

$$e^- + H(1s) \rightarrow H^{-*} \rightarrow e^- + H(1s). \qquad (7\text{-}4)$$
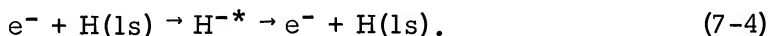
It is also possible to form a metastable state in a "production" experiment. In this case, the metastable system is produced in a collision along with other particles. One simple case is where the target is itself excited to a metastable state

$$A + B \rightarrow A + B^*. \qquad (7\text{-}5)$$

The unstable complex formed, B^*, will subsequently decay,

$$B^* \rightarrow C + D. \qquad (7\text{-}6)$$

In this example, the resonance can be detected by measuring the loss in energy of the scattered particle A, which is equal to the difference in energy of B and B^*. If the resonant state, B^*, is long lived the uncertainty in its energy will be small and the energy loss is correspondingly well defined.

The unstable states may be formed, or may decay, by a radiative process. A particular case occurs when states of helium are formed in which both electrons are excited, such as in the $^1P(2s, 2p)$ state. The doubly excited helium atom may decay either into the ground state of He^+ ejecting an electron or else, through radiation, to the ground state of helium:

$$He^*(2s, 2p) \nearrow He^+(1s) + e^- \qquad (7\text{-}7a)$$
$$\searrow He(1s, 2s) + h\upsilon. \qquad (7\text{-}7b)$$
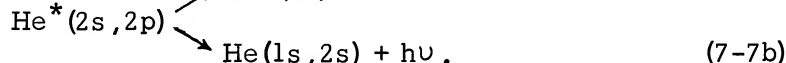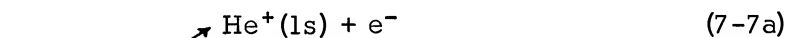
These two processes are in competition, but the probability of the radiationless decay or "auto-ionization" of helium is much greater than that for the radiative decay. This means that the width of the spectral line observed, which is the sum of the partial widths for transitions into each of the channels, is much greater than would be expected for an emission line.[2]

---

[2] The general formulae for resonant and non-resonant scattering developed in Chapter 4 in terms of the reaction matrix may be used to discuss the situation in which a radiative channel is open. A channel with a photon rather than an electron, such as (7-7b), can be treated on the same footing as any other open channel.

It was by observing the broadened emission lines in the vacuum ultra-violet spectrum of helium that the existence of double excited auto-ionizing states was first established[3] (Compton and Boyce, 1928; Kruger, 1930).

These doubly excited helium states were observed again a few years later in electron scattering experiments by Whiddington and Priestly (1934). This early work has been repeated more recently by Silverman and Lassetre (1964) and Simpson (1964), again using electrons as the incident particles, while Rudd (1964, 1965) and others have excited the same states
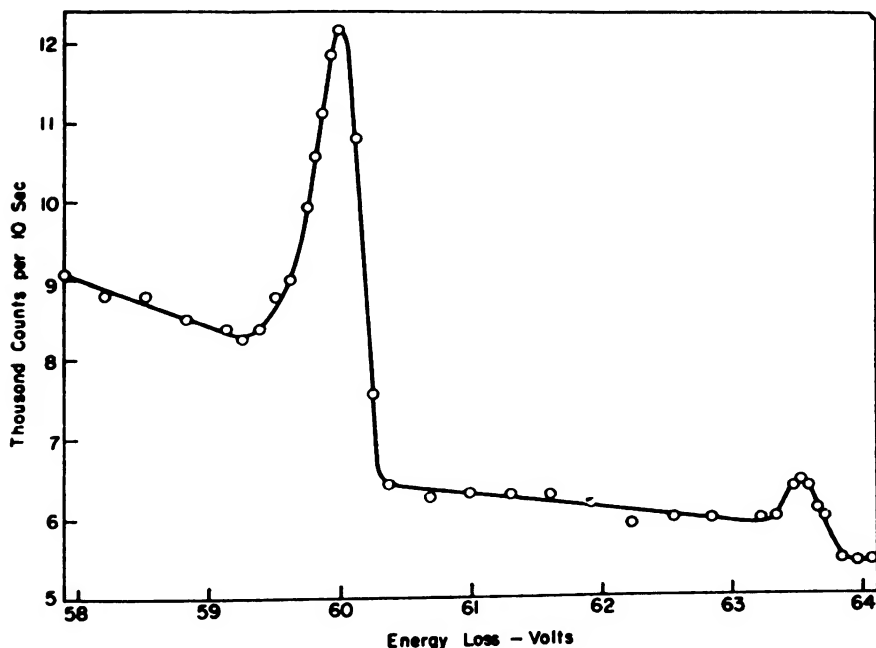
Figure 7-1. The energy loss spectrum of 500 ev electrons scattered by helium (Silverman and Lassetre, 1964).

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[3] Another phenomenon of the same nature as auto-ionization is the Auger effect (Auger, 1925; Burhop, 1952). This occurs following the ionization of an inner shell electron. The resulting ion is unstable and suffers a radiationless decay through the ejection of an electron.

using heavy particles as projectiles. In Fig. 7-1, two peaks
are shown in the energy loss spectrum of 500 ev electrons
scattered by helium, occurring at energies of 60.0 ± 0.1 and
63.5 ± 0.1 ev above the ground state of helium.

By treating the doubly excited states as if they were
stable, it is possible to use the Rayleigh-Ritz variational
method to estimate the corresponding energies. Early work
showed that series of states with different configurations
might be expected to exist. States of the type (2s,ns) or
(2s,np), (2p,ns) and (2p,np) would be among the lowest
lying. In a series such as (2s,ns), as n increases, the
energy of the system must increase until eventually the situa-
tion is reached in which one electron occupies the 2s state of
the helium ion $He^+(2s)$ and the other is free. In other words,
the doubly excited states (2s,ns) converge on the threshold
for electron scattering by the (2s) state of He^+. It would
then be expected that a corresponding series of resonances
would occur in the elastic scattering of electrons by helium
ions below the n = 2 threshold. In the same way, similar
series of states such as (3s,ns), (3p,ns) exist below the
n = 3 threshold for elastic scattering by He^+ and, in general,
below higher thresholds. That series of auto-ionizing states
do exist was clearly shown in the photon absorption experi-
ments of Madden and Codling (1963, 1965) who radiated helium
with ultraviolet light, in the region 100-600 Å, arising from a
180 Mev electron synchrotron. Superimposed on the uniform
absorption spectrum due to the ionization of helium was a series
of 21 discrete lines lying at energies which could be grouped
into series converging on the n = 2, 3 and 4 states of He^+.
In optical absorption, as the ground state of helium is ^1S, the
final state must be ^1P. Two of the series converge on the
n = 2 state of He^+ and must be associated with configurations
(2s,np), (2p,ns). As the lowest state of both series is the
same (2s,2p), and as in the absence of the electron-electron
interaction the states (ns,mp) and (ms,np) are degenerate,
the two series mix and because of this a better set of hydro-
genic basis functions is

$$\Psi_{\pm}(mn) = \frac{1}{\sqrt{2}} [\varphi(ns)\varphi(mp) \pm \varphi(ms)\varphi(np)]. \qquad (7-8)$$

For each value of n there will be two series, which may be
denoted by $^1P(ps,nm+)$ and $^1P(ps,nm-)$. The energies and

Table 7-1

The ^1P auto-ionizing levels in helium, observed by Madden and Codling (1965)

Series converging on the n = 2 level of He$^+$ (65.4 ev)*

Level (n, m)	Position* (ev)	Width (ev)
(2,2)+	60.13	0.172
(2,3)+	63.66	0.83
(2,4)+	64.47	--
(2,5)+	65.01	--
(2,3)-	62.70	--
(2,4)-	64.15	--
(2,5)-	64.67	--

Series converging on the n = 3 and n = 4 levels of He$^+$

(n, m)	Position* (ev)	(n, m)	Position* (ev)
(3,3)+	69.95	(4,4)+	73.77
(3,4)+	71.67	(4,5)+	74.65
(3,5)+	72.21	(4,6)+	75.01
(3,6)+	72.48		
(3,7)+	72.62		
(3,8)+	72.71		

(*Level positions are given in terms of the incident energy.)

classification of the states observed by Madden and Codling for n = 2, 3 and 4 are shown in Table 1, together with the widths where these could be measured.

Scattering experiments, in which the energy loss of the projectile is measured, can detect not only the optically allowed states but also the forbidden states, such as the $^1S(2s)^2$ state, and measurements have demonstrated several series of levels belonging to ^1S and ^3P states. Rudd (1964), and Rudd and Lang (1965) have observed $^1S(2s)^2$ at 57.82 ev, $^1S(2p)^2$ at 62.15 ev, $^1S(1s,3s)$ at 62.95 ev, $^3P(2s,2p)$ at 58.24 ev and so on (see also Simpson et al., 1964).

The resonances predicted by the theory in electron-hydrogen atom scattering are due to the formation of double

excited states of H^-. Some of these resonances have been
confirmed in "formation" experiments carried out in the elastic
scattering region (Schultz, 1964; Kleinpoppen and Raible, 1965).
Similar experiments on both the elastic and inelastic scattering
of electrons by He have shown that several unstable states of
the negative helium ion He^-. In elastic scattering a resonance
at 19.3 ev just below the $n = 2$ threshold (Schultz, 1963) is
assigned to a ^2S state with the mixed configuration
$(1s, 2s^2) + (1s, 2p^2)$ and inelastic scattering experiments have
shown resonance effects in the $2^1S \rightarrow 2^3S$ excitation cross
section and also that levels of He^- exist below the $n = 3$ and
$n = 4$ levels of He.[4]

Atoms other than hydrogen and helium

Auto-ionizing levels are known from spectroscopic and
scattering experiments in many atomic and molecular systems.
As an example, the rare gases Ne, Ar, Kr and Xe all exhibit
series of levels like those in He while resonances have been
shown to be of importance in electron scattering by H_2 and N_2.
The spectroscopic evidence has been reviewed recently by
Garton (1966) and the scattering experiments are discussed in
the reviews of Smith (1966) and Burke (1965).

7-2   CALCULATION OF POSITIONS AND WIDTHS OF RESO-
NANT STATES

There are many ways in which the theory of resonant
states may be developed. We shall not attempt to survey the
very extensive literature that has grown up, but one or two   .
methods that allow calculations to be made of the positions
and widths of the states will be outlined.

Let us return to the problem, discussed in Chapter 5,
of electron scattering by atoms at energies below the first ex-
citation threshold. The wave function is divided into a part
$\mathbf{P}\Psi$ containing the open channel and $\mathbf{Q}\Psi$ containing the closed
channels. It was shown that $\mathbf{P}\Psi$ and $\mathbf{Q}\Psi$ satisfy the coupled
equations,

$$\mathbf{P}(H - E)\mathbf{P}\Psi = -\mathbf{P}H\mathbf{Q}\Psi, \tag{7-9a}$$

$$\mathbf{Q}(H - E)\mathbf{Q}\Psi = -\mathbf{Q}H\mathbf{P}\Psi. \tag{7-9b}$$

In these equations $\mathbf{P}$ is an operator projecting out the (single)

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[4] Schultz and Philbruck (1964), Chamberlain (1965), Chamberlain and Heideman (1965).

open channel, $P^2 = P$ and

$$Q = 1 - P, \quad QP = PQ = 0. \tag{7-10}$$

Roughly speaking, two types of resonance may arise in discussing these equations. The potential in the single channel wave equation

$$P(H - E)P\Psi = 0$$

may have the strength and shape necessary to support a resonant state of the kind discussed in Chapter 1. We shall call this a shape resonance. Alternatively, as discussed in Chapter 5, resonances occur at energies associated with the discrete eigenvalue spectrum of the operator QHQ, that describes the closed channel system. Clearly situations intermediate in character may also occur. Because the resonances discussed in the previous paragraph are usually of the second type, and may be identified with the virtual bound state resonances[5] introduced in Chapter 4, we shall discuss how to calculate the parameters of a resonance in this case, using a formalism developed by Feshbach and applied to the atomic situation by O'Malley and Geltman (1965).

Our starting point will be the expansion of the optical potential in terms of the eigenfunctions of the operator QHQ, given by equations (5-98) to (5-102). Suppose that the total energy E is close to one particular eigenvalue of (QHQ), then the corresponding term in V_p, which is a rapidly varying function of energy, can be separated from the remainder of V_p by writing the equation for $P\Psi$ as

$$(H' - E)P\Psi = - \frac{PH|\varphi_s\rangle\langle\varphi_s|HP}{E - \epsilon_s} P\Psi, \tag{7-11}$$

where

$$H' = PHP + \sum_{n\neq s} \frac{PH|\varphi_n\rangle\langle\varphi_n|HP}{E - \epsilon_n}. \tag{7-12}$$

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[5] These are often called Feshbach resonances in the literature. Shape resonances also play an important role in atomic phenomena, occurring in the vibrational excitation of molecular hydrogen by electrons (Bardsley et al., 1966).

In Chapter 3, section 3-2, the problem of scattering by the sum of two potentials was discussed. This theory can be applied here, taking

$$\bar{V}_p = \frac{P H |\varphi_s \rangle \langle \varphi_s | H P}{E - \epsilon_s} , \qquad (7\text{-}13)$$

as one of the potentials, and the remainder of the interaction as the other. Then as in equation (3-60), the solution of (7-11) can be written as

$$| P \Psi \rangle = | \chi \rangle + G_1 \bar{V}_p | P \Psi \rangle \qquad (7\text{-}14a)$$

$$= | \chi \rangle + (E - \epsilon_s)^{-1} G_1 P H | \varphi_s \rangle \langle \varphi_s | H | P \Psi \rangle, \quad (7\text{-}14b)$$

where $| \chi \rangle$ is the solution of

$$(H' - E) | \chi \rangle = 0 , \qquad (7\text{-}15)$$

and the Green's function G_1 satisfies

$$(H' - E) G_1 = -\mathbf{1} . \qquad (7\text{-}16)$$

The boundary conditions imposed will be different from those assumed in section 3-2. We shall use an angular momentum representation and standing wave boundary conditions so that

$$\chi(\mathbf{x}, \mathbf{r}) \sim r^{-1} X(\mathbf{x}) \sqrt{\frac{2\pi}{k}} \sin\left(kr - \frac{\ell\pi}{2} + \delta_\ell\right) Y_{\ell,m}(\theta, \varphi),$$
$$(7\text{-}17)$$

where $\mathbf{x}$ denotes collectively the internal coordinates of the target, (r, θ, φ) are coordinates of the scattered particle and the internal wave function of the target has been denoted by $X(\mathbf{x})$.

The Green's function G_1 is also chosen to satisfy the standing wave boundary conditions, so that for large r,

$$G_1(\mathbf{x}, \mathbf{r}; \mathbf{x}', \mathbf{r}') \sim -\sqrt{\frac{2\pi}{k}} X(\mathbf{x}) Y_{\ell,m}(\theta, \varphi) \frac{\cos(kr - \ell\pi/2 + \delta_\ell)}{r} \cdot \chi(\mathbf{x}', \mathbf{r}').$$
$$(7\text{-}18)$$

The potential $\tilde{V}_p$ is separable so that an exact solution of (7-14) can now be found. Multiplying (7-14b) on the left by $\langle \varphi_s | H$, we see that

$$\langle \varphi_s | H | \mathbf{P} \Psi \rangle = \langle \varphi_s | H | \chi \rangle + \frac{\langle \varphi_s | H \mathbf{P} G_1 \mathbf{P} H | \varphi_s \rangle \langle \varphi_s | H | \mathbf{P} \Psi \rangle}{E - \epsilon_s} .$$
(7-19)

Solving this equation for $\langle \varphi_s | H | \mathbf{P} \Psi \rangle$

$$\langle \varphi_s | H | \mathbf{P} \Psi \rangle = \frac{\langle \varphi_s | H | \chi \rangle}{1 - (E - \epsilon_s)^{-1} \langle \varphi_s | H \mathbf{P} G_1 \mathbf{P} H | \varphi_s \rangle} , \quad (7-20)$$

enables equation (7-14b) to be written as

$$| \mathbf{P} \Psi \rangle = | \chi \rangle + \frac{G_1 \mathbf{P} H | \varphi_s \rangle \langle \varphi_s | H | \chi \rangle}{E - \epsilon_s - \Delta_s} , \quad (7-21)$$

where Δ_s is defined as

$$\Delta_s \equiv \langle \varphi_s | H \mathbf{P} G_1 \mathbf{P} H | \varphi_s \rangle . \quad (7-22)$$

The asymptotic form of $\mathbf{P} \Psi$ can now be determined with the help of (7-17) and (7-18):

$$\mathbf{P} \Psi \underset{r \to \infty}{\sim} X(\mathbf{x}) \sqrt{\frac{2\pi}{k}} \; r^{-1} \left[\sin\left(kr - \frac{\ell\pi}{2} + \delta_\ell\right) + \cos\left(kr - \frac{\ell\pi}{2} + \right. \right.$$

$$\left. \left. + \delta_\ell \right) \tan \eta_\ell \right] Y_{\ell, m}(\theta, \varphi) , \quad (7-23)$$

where

$$\tan \eta_\ell = - \frac{\Gamma_s / 2}{E - \epsilon_s - \Delta_s} , \quad (7-24)$$

and

$$\frac{\Gamma_s}{2} = | \langle \chi | H | \varphi_s \rangle |^2 . \quad (7-25)$$

The phase shift η_ℓ resonates as E passes through the energy

E_{r}, where $E_{r} = (\epsilon_{s} + \Delta_{s})$, and Δ_{s} has the significance of a level shift, while the level width is Γ_{s}. Combining the terms in (7-23), we see that

$$\mathbf{P}\Psi \sim X(\mathbf{x}) \sqrt{\frac{2\pi}{k}} \frac{1}{\cos \eta_{\ell}} r^{-1} \sin\left(kr - \frac{\ell\pi}{2} + \delta_{\ell} + \eta_{\ell}\right) Y_{\ell,m}(\theta,\varphi).$$

$$(7-26)$$

The total phase shift is $(\delta_{\ell} + \eta_{\ell})$, from which we see that the partial cross section of order ℓ is

$$\sigma_{\ell} = \frac{4\pi(2\ell + 1)}{k^2} \sin^2 (\delta_{\ell} + \eta_{\ell}). \qquad (7-27)$$

A complete calculation of the parameters of a resonance requires the eigenvalue ϵ_{s} of $(\mathbf{QHQ})$, the level shift Δ_{s} from (7-22) and the width Γ_{s} from (7-25).

If it is assumed that the level shifts are small, then a calculation of the eigenvalues of $(\mathbf{QHQ})$ will determine the resonance energies. This eigenvalue problem can be solved by the Rayleigh-Ritz method provided that the trial function φ_{s} is orthogonal to the ground state of the target and does not contain part of the open channel. O'Malley and Geltman have determined in this way the energies[6] of a large number of the $^{1,3}S$ and $^{1,3}P$ states of H^- and of He. The results for the ^1P series of doubly excited He states are shown in Table 7-2. It is seen that the agreement with the experimental results shown in Table 7-1 is good. Also included in Table 7-2 are the results of the close coupling calculations[7] (1s – 2s – 2p) of Burke and McVicar (1965). In these calculations the total phase shift is obtained as a function of energy so that both the

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[6] Other calculations by Lipsky and Russek (1965) and Altick and Moore (1965) are in good agreement with those of O'Malley and Geltman.

[7] In the close coupling calculations and in the theory of this section, where electron scattering by charged ions is discussed (as in $e^- + He^+$), plane waves (where they occur) must be replaced by the appropriate Coulomb waves.

resonance energy E_r and the width Γ can be found directly.
The agreement with experiment is extremely good.

Table 7-2

Calculated positions and widths of ^1P states in helium

	O'Malley and Geltman (1965)	Burke and McVicar (1965)	
^1P	ϵ_s (ev)	E_r (ev)	Γ (ev)
(2s, 2p)	60.19	60.27	0.044
(2s, 3p − 2p, 3s)	62.82	62.77	0.00014
(2s, 3p + 2p, 3s)	63.88	63.69	0.0087
(2s, 4p − 2p, 4s)	64.20	64.11	5.0×10^{-5}
(2p, 3d)	64.43	64.12	1.5×10^{-6}

In the close coupling calculations of Burke and McVicar, the predicted states of doubly excited helium include the ^3P, ^1P and ^3S. More recently this work has been extended in order to determine the D states that lie below the n = 2 level (Cooper et al., 1967). In this case as well, good agreement is obtained with the experimental results, which have been analyzed by Altick and Moore (1967).

The auto-ionizing states of He$^-$, that give rise to resonances near the n = 2 threshold in electron scattering by helium, have been discussed in the close coupling approximation (Burke et al., 1966, 1967). In this work, in order to describe the polarization of the 2^1S and 2^3S states of helium in the field of the incident electron, it is important to include the 2^1P and 2^3P states in the close coupling wave function. The $2^{1,3}P$ states lie close in energy to the $2^{1,3}S$ states (see Table 7-3), and the effect of polarization is large.

These four states, together with the ground state, were included in the expansion, using Hartree-Fock wave functions. The results of the calculations showed that in addition to the ^2S state of He$^-$ at 19.3 ev, ^2P and ^2D states also occur at 20.2 ev (width 0.52 ev) and 21.0 ev (width 0.4 ev) respectively.

Table 7-3

The first four excited states of helium

State	Energy (atomic units)
$^1S(1s, 2s)$	2.1753
$^3S(1s, 2s)$	2.1461
$^1P(1s, 2p)$	2.1332
$^3P(1s, 2p)$	2.2217

These resonances have been observed by Chamberlain and Heideman (1965) in experiments on the inelastic scattering of electrons by helium in the forward direction.

Further calculations were carried out in which just the four excited states of He were included in the expansion and further resonances attributed to the ^2F, ^2G and ^2H levels of He$^-$ were discovered. The cross sections for transitions between the excited states of helium are shown in Fig. 7-2. Analysis shows that these cross sections are dominated by the level structure of He$^-$. The three peaks in the $2^3S - 2^1S$ cross section are caused by the ^2S, ^2P and ^2D resonances, and the steep rise and peaking of all the other cross sections are also due to the effect of the various resonances in varying proportions.

Line profiles

As we have seen, a resonant state may be formed by photon absorption. In this case, the shape of the absorption line can be studied (Fano, 1961, O'Malley and Geltman, 1965). The radiative part of the interaction is always given accurately by perturbation theory, so that the transition probability for the reaction

$$h\nu + A \rightarrow A^{**} \rightarrow A^* + e,$$

is proportional to a matrix element of the form

$$\langle i | T | \Psi_f \rangle, \tag{7-28}$$

where Ψ_f is the wave function for the final state of the system
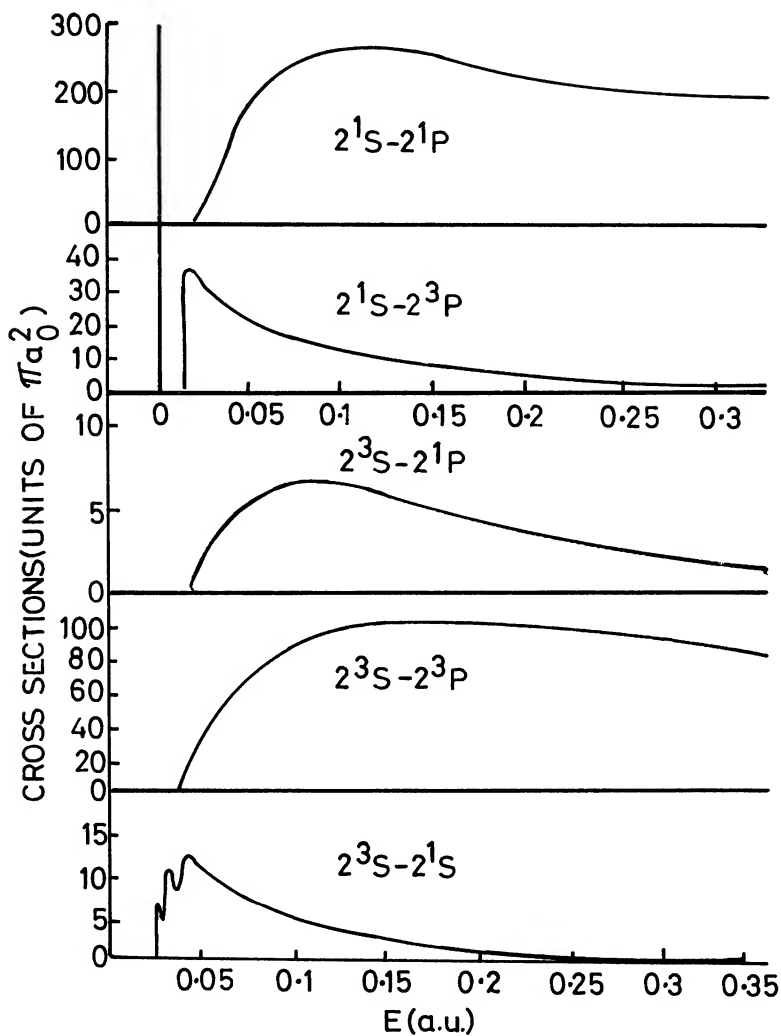
Figure 7-2. Cross sections for transitions among the $n = 2$ levels of helium induced by electron impact, calculated in a close coupling approximation (Burke et al., 1967).

and $\langle i |$ is the initial state, T being the transition operator. The final state wave function is just the one we have considered except that the normalization of $\mathbf{P}\Psi$ required in (7-28) differs from that assumed in (7-26) by the factor $1/\cos \eta_\ell$. We need then

$$\mathbf{P}|\Psi_f\rangle = \cos \eta_\ell |\mathbf{P}\Psi\rangle = \cos \eta_\ell |\chi\rangle - \sin \eta_\ell |\Psi_1\rangle, \quad (7\text{-}29)$$

where, using (7-21), (7-24) and (7-25), $|\Psi_1\rangle$ is defined as

$$|\Psi_1\rangle = \frac{G_1 \mathbf{P} H |\varphi_s\rangle}{\langle \chi | H | \varphi_s \rangle} . \quad (7\text{-}30)$$

Neither $|\chi\rangle$ nor $|\Psi_1\rangle$ are rapidly varying functions of energy and, if the resonance is narrow, these functions may be treated as energy independent, the energy variation being concentrated in the factors $\sin \eta_\ell$ and $\cos \eta_\ell$. To obtain Ψ_f we also need $\mathbf{Q}\Psi_f$. This can also be split into parts containing $\sin \eta_\ell$ and $\cos \eta_\ell$ as factors, and O'Malley and Geltman show that $\Psi_f = \mathbf{P}\Psi_f + \mathbf{Q}\Psi_f$ can be written as

$$\Psi_f = \Psi_0 \cos \eta_\ell - \bar{\Psi}_1 \sin \eta_\ell, \quad (7\text{-}31)$$

where

$$|\Psi_0\rangle = |\chi\rangle + \sum_{n \neq s} \frac{|\varphi_n\rangle \langle \varphi_n | \mathbf{Q} H | \chi \rangle}{(E - \epsilon_n)}, \quad (7\text{-}32)$$

$$|\bar{\Psi}_1\rangle = \frac{|\varphi_s\rangle + G_1 \mathbf{P} H |\varphi_s\rangle}{\langle \chi | H | \varphi_s \rangle} +$$

$$+ \sum_{n \neq s} \frac{1}{\langle \chi | H | \varphi_s \rangle} (E - \epsilon_n)^{-1} |\varphi_n\rangle \langle \varphi_n | \mathbf{Q} H \mathbf{P} G_1 \mathbf{P} H \mathbf{Q} |\varphi_s \rangle.$$

In terms of the resonance parameters, $\sin \eta_\ell$ and $\cos \eta_\ell$ are

$$\sin \eta_\ell = \frac{(\Gamma_s/2)}{\left[(E - \epsilon_s - \Delta_s)^2 + 1/4 \, \Gamma_s^2\right]^{1/2}} \quad (7\text{-}33)$$

$$\cos \eta_\ell = \frac{(\epsilon_s + \Delta_s - E)}{\left[(E - \epsilon_s - \Delta_s)^2 + 1/4 \, \Gamma_s^2\right]^{1/2}} \, ,$$

from which

$$\langle i|T|\Psi_f \rangle = \frac{\left[(\epsilon_s + \Delta_s - E)\langle i|T|\Psi_0 \rangle - 1/2 \, \Gamma_s \langle i|T|\Psi_1 \rangle\right]}{\left[(E - \epsilon_s - \Delta_s)^2 + 1/4 \, \Gamma_s^2\right]^{1/2}} \, .$$

$$(7\text{-}34)$$

Well away from the resonance the transition probability is given by the amplitude $\langle i|T|\Psi_0 \rangle$, so that the ratio of the transition probability over the resonance region to the non-resonant background is

$$\left| \frac{\langle i|T|\Psi_f \rangle}{\langle i|T|\Psi_0 \rangle} \right|^2 = \frac{(\epsilon + q)^2}{1 + \epsilon^2} \, , \qquad (7\text{-}35)$$

where

$$\epsilon = -\cot \eta_\ell = \frac{E - \epsilon_s - \Delta_s}{1/2 \, \Gamma_s}; \quad q = \frac{\langle i|T|\Psi_1 \rangle}{\langle i|T|\Psi_0 \rangle} \, . \qquad (7\text{-}36)$$

Burke and McVicar (1965) have calculated q and ϵ for the photo-ionization of helium using the close-coupling wave functions in the (1s – 2s – 2p) approximation; an elaborate variational wave function was used for the initial helium ground state. The shape of the absorption line for the $(2s2p)^1 P$ resonance is shown in Fig. 7-3; it is in close agreement with the observed line given by Madden and Codling (1965). The quantity plotted in Fig. 7-3 is the oscillator strength for the transition (df/dE), which is related to the cross section by

$$\frac{df}{dE} = \frac{1}{4\pi^2 a} \, \sigma ,$$

where a is the fine structure constant. The limit of (df/dE) for large ϵ is denoted by $(df/dE)_0$, so that

$$\frac{df}{dE} = \left(\frac{df}{dE} \right)_0 \frac{(\epsilon + q)^2}{(1 + \epsilon^2)} \, .$$

The calculated value of $(df/dE)_0$ was 0.1710. A zero in the cross section occurs when $\epsilon + q = 0$, and whether this zero occurs above or below the resonance position $(\epsilon = 0)$ depends
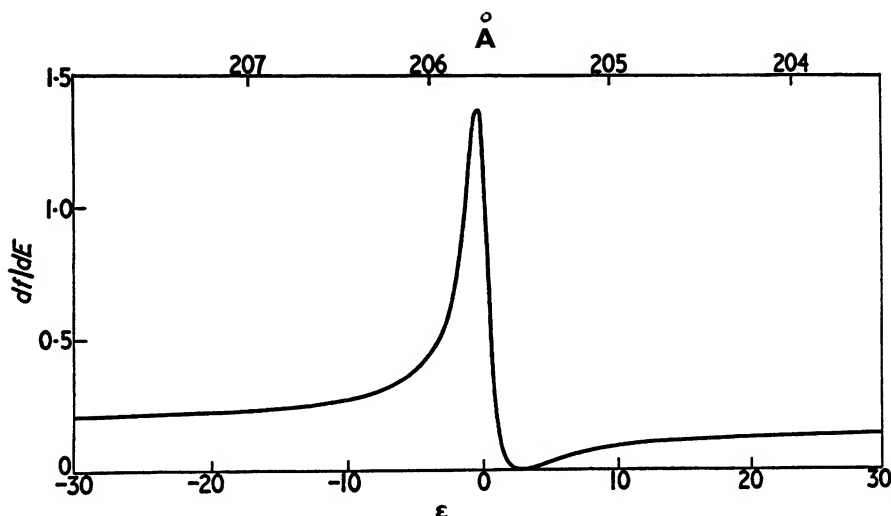
Figure 7-3.   The shape of the absorption line associated with the (2s2p) ^{1}P double excited state of helium (Burke and McVicar, 1965).

on the sign of q.   In the case shown in Fig. 7-3, q = -2.5 so that the zero is above the point of maximum absorption.   The maximum absorption does not occur at the resonance position (ϵ = 0), but, as can be seen from (7-35), at the position ϵ = 1/q.   If the energy for which this occurs is E_m, then

$$E_m = \epsilon_s + \Delta_s + \frac{\Gamma_s}{2q} .$$ (7-37)

Many channel scattering

The theory presented above may be generalized to cover the case where several channels are open at the resonance energy.   That this is a case of importance is seen from the fact that series of resonances occur below the higher thresholds in hydrogen, helium and other systems.   In Chapter 4, the general form of the transition matrix was obtained near energies at which one eigenphase shift passes through $\pi/2$.   From these formulae the effect of a resonance on not only the elastic scattering but also on the excitation threshold can be discussed. A case of importance concerns the influence of the resonances

below the $n = 3$ threshold in $e^- - H$ scattering on the $n = 1$
to $n = 2$ excitation cross section. This has been studied in
detail by Burke et al. (1966) and by Macek and Burke (1967),
but the analysis is too lengthy to be given here.

If the forces are of short range, the behavior of the
cross section near a threshold can be obtained from the general
expressions (4-100) and (4-101). If the eigenphase shift Δ_0
is resonant just above a certain threshold β, then the excita-
tion cross section $\sigma_{\beta a}$ is

$$\sigma_{\beta a} \propto \frac{\gamma_a \gamma_\beta}{(E_r' - E) - i\gamma/2} ,$$

where the width γ_β is proportional to $k_\beta^{2\ell+1}$. (Notice that the
energy variation of the eigenphases and the parameters $R_{a\beta}$
near a threshold, follows from (4-110)). The excitation cross
section is then proportional to the partial width in channel a.
If the resonance is just below the open threshold, the excita-
tion cross section is still proportional to the partial width of
the resonance in the incident channel. If there are only two
channels, then $\sigma_{\beta a}$ is just proportional to the total width.
This can be shown by using the **M** matrix extrapolation through
the threshold. In general, the existence of one or more reso-
nances below a threshold leads to a rapidly rising or peaked
excitation cross section and the rate of rise is proportional to
the width of the resonance.

The Herzenberg-Mandl resonance theory

The projection operator technique outlined earlier in
this chapter is not the only method that can be employed in the
description of resonant states. An alternative approach, origi-
nally used in the theory of nuclear reactions, is to locate the
position of the resonances by looking for the eigenvalues of
the complete Hamiltonian when certain modified boundary con-
ditions are imposed (Kapur and Peierls, 1937). This approach
has been modified by Herzenberg and Mandl (Herzenberg and
Mandl, 1963; Herzenberg, Kwok and Mandl, 1964a,b; Mandl,
1967) to a form more suitable for atomic calculations, where
long range potentials are encountered. This formulation has
the advantage that no distinction is made between the Feshbach

or virtual bound state resonances, discussed earlier and the
shape resonances, that are not associated with bound states
of the closed channel Hamiltonian (QHQ).

For the case of simplicity, the identity of the scattered
and target particles will be ignored in the following discussion.
There is no difficulty in treating exchange and rearrangement,
and in the original papers these effects are displayed explic-
itly.

The complete Schrödinger equation for the system of the
incident electron and target atom is

$$(H - E)\Psi = 0,\tag{7-38}$$

and a solution is required of the form

$$\Psi_a^+ = \varphi_a + \Psi_a^S,\tag{7-39}$$

where φ_a is the incident unperturbed wave function. φ_a satis-
fies the equation

$$(H_a - E)\varphi_a(\mathbf{r},\mathbf{x}) = 0$$

and is of the form (see 4-7 and 4-43)

$$\varphi_a(\mathbf{r},\mathbf{x}) = \exp(i\mathbf{k}_a \cdot \mathbf{r})X_a(\mathbf{x}),\tag{7-40}$$

where $X_a(\mathbf{x})$ is a target eigenfunction that is normalized and
belongs to the eigenvalue ϵ_a and as usual $\mathbf{x}$ denotes all the
coordinates of the target. The total energy E is then given by

$$E = \frac{\hbar^2}{2m}k_a^2 + \epsilon_a.\tag{7-41}$$

The function Ψ_a^S satisfies the equation

$$(H - E)\Psi_a^S = -[H - E]\varphi_a = -V_a\varphi_a,\tag{7-42}$$

where V_a is the interaction between the incident electron and
the target atom. The boundary condition to be imposed on
$\Psi_a^S(\mathbf{r},\mathbf{x})$ is that it shall contain only outgoing waves, and for
energies E which are below the ionization threshold of the
target, we have (see equation 4-47a) that:—

$$\Psi_a^S(\mathbf{r},\mathbf{x}) \sim \sum_\beta T_{\beta a}(E)\left(\frac{2m}{\hbar^2}\right)\frac{1}{4\pi} X_\beta(\mathbf{x})\frac{e^{ik_\beta r}}{r}, \qquad (7\text{--}43)$$

where the transition matrix for scattering in which the target is excited from the state a to the state β is (4-47b)

$$T_{\beta a}(E) = \int \varphi_\beta^*(\mathbf{r},\mathbf{x})V_\beta \Psi_a^+(\mathbf{r},\mathbf{x})d\mathbf{r}d\mathbf{x}$$

$$= T_{\beta a}^B(E) + \int \varphi_\beta^*(\mathbf{r},\mathbf{x})V_\beta \Psi_a^S(\mathbf{r},\mathbf{x})d\mathbf{r}d\mathbf{x}, \qquad (7\text{--}44)$$

and in the second line $T_{\beta a}^B$ is the Born approximation:

$$T_{\beta a}^B(E) = \int \varphi_\beta^*(\mathbf{r},\mathbf{x})V_\beta \varphi_a(\mathbf{r},\mathbf{x})d\mathbf{r}d\mathbf{x}. \qquad (7\text{--}45)$$

In Chapter 1, it was explained that the resonant states were associated with points at which scattering amplitudes possess a pole at some complex energy $E = W - i\Gamma/2$. At the pole position the wave function satisfies a purely outgoing wave boundary condition. Such a state with purely outgoing waves is called a Siegert state (Siegert, 1939) and we shall try to obtain such states directly from the Schrödinger equation (7-38). For real values of E, equation (7-38) does not possess solutions with purely outgoing waves, but it is possible to modify the equation in such a way that such solutions exist at discrete real values of E. The modified equation is

$$[K + V_A + \mu(E)V_B - E]\Psi_n = 0, \qquad (7\text{--}46)$$

where K is the kinetic energy operator, so that

$$H = K + V.$$

The potentials V_A and V_B represent a division of the original potential energy operator V, such that when the parameter μ is equal to unity, the equation reduces to the original Schrödinger equation; that is

$$V = V_A + V_B. \qquad (7\text{--}47)$$

For fixed real E, we have an eigenvalue problem for the scaling parameter $\mu(E)$, if outgoing wave boundary

conditions are imposed on the wave function Ψ_n. In general, for each value of E there will be a set of discrete complex eigenvalues $\mu_n(E)$, and the associated eigenfunctions Ψ_n will form a complete set. The problem as stated is not completely consistent, as for a range of values of μ, the target will become unbound and the eigenfunctions will no longer satisfy the required boundary conditions. This difficulty can be overcome by requiring that when any of the electrons exceeds a certain distance R from the origin, the potential reduces to the original potential V. To do this we set

$$V_A = (1 - \Theta)V$$

$$V_B = \Theta V,$$
\hfill (7-48)

where

$$\Theta = \theta(R - r) \prod_{i=1}^{z} \theta(R - x_i).$$
\hfill (7-49)

As usual, $\theta(y) = 1$ if $y > 0$, $\theta(y) = 0$ if $y < 0$ and $\mathbf{r}$ is the position vector of the incident electron and $\mathbf{x}_i$ is the position vector of the ith bound electron. When the electrons are all within a sphere of radius R, the potential is equal to μV, but when any of the electrons is outside this sphere the potential takes on its original value V. In this respect, the theory differs from the Kapur-Peierls method. In that method, developed for problems in nuclear physics with short range potentials, the potential energy was assumed to vanish outside the radius R. This is an unsatisfactory approximation when the potentials are of long range.

To specify the outgoing states more completely we shall use an angular momentum basis for the scattered particle. Then any of the functions $\Psi_n(\mathbf{r},\mathbf{x})$ can be expanded in the set of target eigenfunctions

$$\Psi_n(\mathbf{r},\mathbf{x}) = \sum_{\gamma} X_{\gamma}(\mathbf{x}) Y_{\ell_{\gamma},m_{\gamma}}(\theta,\varphi) \frac{1}{r} f_{\ell_{\gamma}}(r).$$
\hfill (7-50)

The radial function of the scattered particle $f_{\ell_{\gamma}}(r)$ must then be of outgoing form. This requires that in the limit $r \to \infty$, we have

$$\frac{d}{dr}\left[\log f_{\ell_\gamma}(r)\right] = F_\gamma(k_\gamma r) = ik_{\gamma'}, \quad r \to \infty, \tag{7-51}$$

where

$$F_\gamma(k_\gamma r) \equiv \frac{d}{dr}\left[\log rh_\gamma^+(k_\gamma r)\right]. \tag{7-52}$$

These conditions, together with the requirement that the functions $f_{\ell_\gamma}(r)$ are regular at the origin, specify the eigenvalue problem completely.

A set of functions $\widetilde{\Psi}_n$ that obey ingoing wave boundary conditions may be defined as the solution of

$$\left(K + V_A + \mu_n^*(E)V_B - E\right)\widetilde{\Psi}_n = 0, \tag{7-53}$$

and then it is easy to show that Ψ_n satisfies the orthonormality conditions,

$$\int \Psi_n^* V_B \Psi_m\, d\mathbf{x}\, d\mathbf{r} = \delta_{nm}. \tag{7-54}$$

To obtain the outgoing wave part of the scattering wave function Ψ_a^+, Ψ_a^S is expanded in the set of functions Ψ_n

$$\Psi_a^S = \sum_n C_n(a)\Psi_n. \tag{7-55}$$

Inserting this expression into (7-42), and using the orthonormality conditions (7-54), we find that

$$[\mu_n(E) - 1]C_n(a) = +\int d\mathbf{r}\int d\mathbf{x}\, \Psi_n^*[H - E]\varphi_a. \tag{7-56}$$

Defining $\gamma_{na}(E)$ as

$$\gamma_{na}(E) \equiv [\mu_n(E) - 1]C_n(a) \tag{7-57a}$$

and

$$\bar{\gamma}_{n\beta}(E) \equiv \left[\mu_n^*(E) - 1\right]C_n^*(\beta). \tag{7-57b}$$

the transition matrix can be calculated from (7-44), (7-55) and (7-56):

$$T_{\beta a}(E) = T^B_{\beta a}(E) + \sum_n \frac{\bar\gamma_{n\beta}(E)\gamma_{na}(E)}{\mu_n(E) - 1} \cdot \tag{7-58}$$

This is exact, but if now the energy E is close to one of the roots of the equation

$$\mu_i(E) = 1 \tag{7-59}$$

with $E = (E_i - i\Gamma_i/2)$, then only one term in the summation in (7-58) will be important and expanding in a Taylor's series

$$T_{\beta a}(E) \approx \Upsilon_{\beta a}(E) + \frac{\bar\gamma_{i\beta}(E_i)\gamma_{ia}(E_i)}{(E - E_i + i\Gamma_i/2)\mu'_i(E)} , \tag{7-60}$$

where $\Upsilon_{\beta a}(E)$ is slowly varying function of E

$$\Upsilon_{\beta a}(E) = T^B_{\beta a}(E) + \sum_{n \neq i} \frac{\bar\gamma_{n\beta}(E)\gamma_{na}(E)}{[\mu_n(E) - 1]} . \tag{7-61}$$

The second term in (7-60) is of typical Breit-Wigner form and represents a resonance with energy E_i and width Γ_i. The parameters μ'_i and Γ_i may be calculated in terms of the functions Ψ_i:

$$\mu'_i = \int d\mathbf{r} \int d\mathbf{x} \left\{ \Psi^*_i \Psi_i + \sum_\gamma \left(\frac{1}{2k_\gamma}\right) \frac{\partial F_\gamma(k_\gamma R)}{\partial k_\gamma} \left(f_{\ell_\gamma}(R)\right)^2 \right\} \tag{7-62a}$$

$$\Gamma_i = \left(\frac{\hbar^2}{m}\right) \frac{\sum_\gamma \left\{ |f_{\ell_\gamma}(R)|^2 \operatorname{Im}F_\gamma(k_\gamma R) \right\}}{\int d\mathbf{r} \int d\mathbf{x} |\Psi_i|^2} . \tag{7-62b}$$

In these expressions, the integration is over the region r < R. For short range interactions μ'_i, Γ_i are independent of R, provided that R is greater than the range of the potential, but for long range interactions μ'_i and Γ_i do depend on R and some modifications of the formulae are necessary, which are discussed in the original papers.

Application

Herzenberg and Mandl have developed a variational method to obtain the eigenvalues of the equation (7-47), and have calculated the position of the auto-ionizing levels in a number of atomic and molecular problems. Herzenberg and Mandl (1963) discussed the s-wave singlet resonance in e^- – H scattering. They were able to find the resonance at 9.6 ev using a very simple trial function: the sum of products of modified hydrogenic functions. In a similar way Kwok and Mandl (1965) were able to obtain the resonance below the excitation threshold in electron helium scattering. Both the calculated position E = 19.5 ev and the width $\Gamma = 0.8 \times 10^{-2}$ to 3×10^{-2} ev agree well with the observations. This formalism has also been used to discuss resonances in the vibrational excitation and dissociative attachment of hydrogen molecules by electron impact. The resonant states are in this case states of the molecular ion H_2^-.

7-3   LONG RANGE FORCES AND RESONANCES NEAR THRESHOLDS

In Chapter 2, it was seen that if the elements of the **K** or **M** matrices are known above a threshold, and using the effective range formula satisfied by **M**, the **K** matrix could be obtained below threshold. If the extrapolated **K** matrix satisfied condition (4-116) at a particular energy, a virtual bound state resonance occurred in the open channels below the particular threshold of interest. The extrapolation of the **M** matrix, discussed in Chapter 4, is valid when the forces are at short range. In many important cases, in electron-atom scattering, the forces are long range and the extrapolation must be modified, but before discussing the modification, it is interesting to examine the case of short range forces in a little more detail. An example has been given by Damburg and Peterkop (1962), who discussed the excitation of the 2s state of hydrogen by electron impact on the ground state. Above the threshold, they calculated the matrix elements of the **M** matrix for the $\ell = 0$ partial wave as a function of energy, in the two state approximation, retaining only the 1s and 2s states of hydrogen in the close-coupling wave function. These matrix elements were fitted to the effective range formula

$$\mathbf{M}(E) = \mathbf{M}(E_0) + (E - E_0)\mathbf{R}_0(E_0), \qquad (7\text{-}63)$$

where E_0 is the threshold energy $(k_0^2 = 0.75)$. The results for triplet and singlet scattering and also in the no-exchange approximation are shown in Table 7-4.

Table 7-4

Elements of the matrices $\quad\mathbf{M}(E_0)\quad$ and $\quad\mathbf{R}_0(E_0)\quad$ for $\quad(1s - 2s)\quad$ excitation of hydrogen

Matrix element	Triplet (s = 1)	Singlet (s = 0)	No exchange
M_{11}	1.13	0.0301	0.9373
M_{12}	-0.0629	-0.0017	-0.3097
M_{22}	-0.356	-0.1206	-0.2043
R_{011}	4.82	1.20	7.64
R_{012}	-4.32	-0.06	-10.68
R_{022}	11.54	5.14	19.2

The transition matrix is given in terms of $\mathbf{M}$ by

$$\mathbf{T} = \frac{\mathbf{K}}{1 - i\mathbf{K}} = \mathbf{k}^{\ell+1/2}\,\frac{1}{\mathbf{M} - i\mathbf{k}^{2\ell+1}}\,\mathbf{k}^{\ell+1/2}, \qquad (7\text{-}64)$$

where $\mathbf{k}$ is a diagonal matrix with elements k_1 and k_2, the channel momenta. Extrapolating below threshold we find poles in $\mathbf{T}$ at the point where

$$\det|\mathbf{M} - i\mathbf{k}^{2\ell+1}| = 0, \qquad (7\text{-}65)$$

that is, where

$$D = (M_{11} - ik_1)(M_{22} - ik_2) - M_{12}M_{21} = 0. \qquad (7\text{-}66)$$

Below threshold we have $k_2 \to iK_2$, where K_2 is real, and

$$\epsilon_0 + \frac{1}{2}k_1^2 = \epsilon_1 - \frac{1}{2}K_2^2, \qquad (7\text{-}67)$$

where ϵ_0 and ϵ_1 are the energies of the ground and first

excited states of hydrogen.

When the coupling between the channels is ignored, the bound state poles in channel 2, that give rise to resonances in channel 1 when the coupling is switched on, must be on the imaginary k_2 axis. The pole positions in the absence of coupling are given by the zero of the equation (in atomic units)

$$M_{22} + (R_0)_{22} \frac{1}{2} k_2^2 - i k_2 = 0. \tag{7-68}$$

Using the figures given in Table 7-4, the zeros for the triplet case do not lie on the imaginary k_2 axis and so do not give rise to resonances. In the singlet case, both zeros are on the imaginary axis and the zero near the origin $(k_2 = 0)$ leads to a narrow resonance in the elastic scattering in channel 1. In the no-exchange case, the zeros are also on the imaginary axis, but the lower zero which is near the threshold $(k_2 = 0)$ lies on the negative real axis. This is an anti-bound state (see Chapter 1) and it gives rise to an increase in scattering near threshold, but not to a resonance below threshold, as the pole produced is on the wrong sheet in the k_1 plane.

The transition matrix below threshold in the first channel is given by

$$T_{11} = k_1 M_{22} D(E) \tag{7-69}$$

and the cross section by

$$\sigma = \frac{4\pi}{k_1^2 + \gamma^2}, \tag{7-70}$$

where

$$\gamma = M_{11} - \frac{|M_{12}|^2}{M_{22} + K_2}.$$

The resonance energy can be defined as the energy for which γ vanishes and σ takes on its maximum value.

Long range forces at degenerate thresholds

The potential terms coupling s and p states are proportional to $1/r^2$ for large r (Chapter 5). In the case of electron scattering by hydrogen atoms, close-coupling equations for the radial wave functions connecting the 2s and 2p levels become asymptotically, for zero total angular momentum,

$$\left[\frac{d^2}{dr^2} + k_2{}^2\right] F_{2s}(r) = -\frac{6}{r^2} F_{2p}(r),$$ (7-71a)

$$\left[\frac{d^2}{dr^2} - \frac{2}{r^2} + k_2\right] F_{2p}(r) = -\frac{6}{r^2} F_{2s}(r).$$ (7-71b)

Because the (2s) and (2p) states are degenerate, the same value of the energy, $k_2{}^2$, appears in both equations. In this case, by taking linear combinations of F_{2p} and F_{2s} the equations can be uncoupled. If the equations are written in matrix form with a potential matrix

$$\mathbf{V}(r) = \frac{1}{r^2}\begin{bmatrix} 0 & -6 \\ -6 & 2 \end{bmatrix},$$ (7-72)

uncoupling the equations is equivalent to diagonalizing V. This can be achieved through the introduction of an orthogonal matrix **A**, such that (Seaton, 1961)

$$(\mathbf{A}^{-1}\mathbf{V}(r)\mathbf{A})_{ij} = \delta_{ij}\lambda_i(\lambda_i + 1).$$ (7-73)

Such a diagonalization can be carried out at any degenerate threshold. In the case of the 2s – 2p threshold, we find that $\lambda(\lambda + 1) = 1 \pm \sqrt{37}$ or

$$\lambda_1 = -\frac{1}{2} \pm \sqrt{\sqrt{37} + 5/4}$$

$$\lambda_2 = -\frac{1}{2} \pm i\sqrt{\sqrt{37} - 5/4}.$$ (7-74)

The form of solution of the Schrödinger equation when the potential is asymptotic to an inverse square power of r was discussed in Chapter 3 and it was shown that an attractive potential (corresponding to λ_2) supports an infinite number of bound states. From (3-79) we see that in the present case ($\gamma^2 < 0$) the wave function is proportional to

$$\cos[\text{Im } \lambda \log r + B].$$ (7-75)

Successive nodes occur at positions r_1, r_2 where

$$\text{Im } \lambda \log\left(\frac{r_1}{r_2}\right) = \pi.$$ (7-76)

For large r, the bound state wave functions become equal to

exp $(-K_2 r)$, where $K_2{}^2 = (ik_2)^2$, and this implies that the ratio in energy of successive levels is

$$R = \frac{r_1{}^2}{r_2{}^2} = \exp\left[\frac{2\pi}{\mathrm{Im}\ \lambda}\right]. \qquad (7\text{-}77)$$

For the 2s - 2p threshold, $R = 17.4$ and the bound states form an infinite sequence just below the threshold. In practice because of the relativistic splitting between the 2s and 2p levels (the Lamb shift) this sequence will not be infinite. For non-zero total angular momentum L, it can be shown that at the $n = 2$ threshold, only the $L = 0$, $L = 1$ and $L = 2$ states possess sequences of levels in this way, but as n increases, more and more values of L possess resonant series. For the higher thresholds there can be more than one series of levels, with different level spacings.

   Because of the coupling to the open channel, the levels below the $n = 2$ threshold become unbound and are meta-stable rather than stable. These metastable states of the complete system at the degenerate levels give rise to the resonances observed beneath the threshold, and in general it is the existence of long range forces that explains the close association of thresholds and sequences of resonances. To make the connection quantitative, the **M** matrix extrapolation procedure has been modified for use in the presence of an inverse square law potential by Gailitis and Damburg (1963). (The case of the Coulomb interaction has also been discussed: Gailitis, 1963; Seaton, 1966).   The **T** matrix is found to be of the form

$$\mathbf{T} = \left[e^{i\pi\ell/2}\,\mathbf{A}\,e^{-i\pi\lambda}\,\mathbf{A}^{-1}\,e^{i\pi\ell/2} - 1\right]\frac{1}{2i} +$$

$$+ e^{i\pi\ell/2}\,\mathbf{A}\,e^{-\pi\lambda/2}\,\mathbf{k}^{\lambda+1/2}\,\cfrac{1}{\mathbf{M} - \cfrac{ie^{-i\pi\lambda}}{\cos\ \pi\lambda}\mathbf{k}^{2\lambda+1}}\,\mathbf{k}^{\lambda+1/2}\,\mathbf{A}^{-1}\,e^{i\pi\ell/2},$$

where **M** is real and symmetric, and is analytic in E through the threshold. As λ is complex, the excitation cross section, which behaves like $k^{2\lambda+1}$, will oscillate above threshold and become finite at threshold. These predictions appear to be in accord with experiment (Chamberlain et al., 1964).

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Chapter 8

FAST COLLISIONS BETWEEN
ATOMS

The theory of the scattering of atoms by atoms is for-
mally similar to that for electron-atom scattering, but there
are important differences of scale and complexity. Because
the projectile is heavy, at practically all velocities for which
scattering experiments can be performed many channels are
open and excitation or ionization of the projectile or target
atom is possible as well as charge transfer. For example, an
electron with an energy of 1 a.u. (27.2 ev), has a velocity
of 3.07×10^8 cm/sec. An atom of atomic weight A, with the
same velocity, possesses an energy of (1837A) a.u. (50 A
kev). For a given velocity not only the energy, but the mo-
mentum $\hbar k$, is much larger for an atomic than for an electronic
collision, and taking the distance of closest approach, r_0, in
a collision to be of the order of 1 a.u., this implies that the
inequality $(kr_0) > 1$ holds down to very low energies. In the
case of proton-hydrogen scattering $kr_0 = 1$ at an energy of
$E = 5.3 \times 10^{-4}$ a.u. $(1.45 \times 10^{-2}$ ev) and for heavier ions the
corresponding energy is even lower. When the condition
$(kr_0) \gg 1$ holds, classical or semiclassical methods will
provide an accurate description of the heavy particle motion,
except for very small angles of scattering $\theta < (1/kr_0)$ and this
will be true for all systems of interest. An exception is the
theory of the viscosity and diffusion of monatomic gases at
low temperatures, for which $(kr_0) \lesssim 1$ and which falls outside
the scope of this book. Classical conditions do not, in gen-
eral, apply to the electronic motion and the probability of a

transition involving electrons must be calculated by the
methods of quantum theory.[1]

8-1   HIGH ENERGY EXCITATION AND CHARGE EXCHANGE

As in the case of electron scattering, at sufficiently
high energies the Born approximation for excitation is expected
to be valid. In Chapter 1, the condition for the validity of the
Born approximation in potential scattering was found to be ·
$a\bar{U}/k \ll 1$, where $\bar{U} = (2m/\hbar^2)\bar{V}$ and $\bar{V}$ was an average of the
potential. It is seen that the condition depends on the veloc-
ity rather than the momentum of the scattered particle, since
$a\bar{U}/k = 2a\bar{V}/\hbar v$. In electron scattering we saw that the Born
approximation became accurate at energies of a few hundred
electron volts, when the velocity of the incident electrons was
some tens of times the orbital velocities of the target electrons.
The corresponding velocities in heavy particle collisions will
be attained at energies of several hundred kev and in this
energy region the Born approximation is expected to provide
accurate results.

We take first the case of scattering of a bare nucleus
of charge Z and mass M_A by an atom of mass M_B. The
cross section in the Born approximation for excitation of the
atom from the state 0 to the state n is (see page 249)

$$\sigma = \int_{K_{min}}^{K_{max}} \frac{8\pi\mu^2}{k_0^2\hbar^4} \frac{Z^2}{K^3} |f_{no}(K)|^2 dK, \tag{8-1}$$

where

$$f_{no}(K) = -\sum_{s=1}^{N} \int e^{iKx_s} X_0 X_n^* d\mathbf{r}. \tag{8-2}$$

The only difference from the corresponding formulae for electron
scattering is that the electron mass is replaced by μ, the re-
duced mass of the system

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[1] A detailed review of the experiments on excitation and electron capture in ion-atom
collisions has been given recently by deHeer (1967b).

$$\mu = \frac{M_A M_B}{M_A + M_B} ,$$

(8-3)

and that an extra factor Z^2 appears.

The limits of the momentum transfer K may be simplified, using the fact that $(\epsilon_0 - \epsilon_n)/\mu$ is small. From the conservation of energy relation

$$\frac{k_0^2}{2\mu} + \epsilon_0 = \frac{k_n^2}{2\mu} + \epsilon_n$$

(8-4)

we have

$$K_{min} = k_0 - k_n \doteq \frac{|\epsilon_0 - \epsilon_n|}{\hbar v} \left[1 + \frac{|\epsilon_0 - \epsilon_n|}{2\mu v^2} \right],$$

(8-5)

and K_{max} can be taken to be infinite. With these simplifications, Bates and Griffing (1953) showed that, considered as a function of velocity, the cross section for proton-atom scattering $(Z = 1)$ approaches the corresponding electron-atom cross section at high velocities,

$$\{\sigma_p(v) - \sigma_e(v)\} \to 0 \quad \text{as} \quad v \to \infty.$$

(8-6)

At lower energies, they also obtained the scaling law

$$\sigma_e(v) = \frac{1}{(1 + \delta)^2} \left(\sigma_p(v_1) - \delta^2 \sigma_p(v_2) \right),$$

(8-7)

where δ, v_1 and v_2 are defined by

$$v_1 = v(1 + \delta)^{-1}, \quad v_2 = \delta v_1$$

$$\delta = \frac{|\epsilon_0 - \epsilon_n|}{2\mu v_1^2} .$$

(8-8)

The cross sections for a large number of atom-atom or ion-atom transitions have been published using the Born approximation and references to the earlier work may be found in Bates (1962) and in Mott and Massey (1965). Except for collisions between ions isoelectronic with hydrogen, the internal wave functions X_n are only known approximately, and as

usual this introduces some uncertainty into the results. If both the projectile and the target are charged ions, the Born approximation can be used without allowing for the residual Coulomb interaction, because at the velocities concerned Coulomb scattering is confined to the forward direction. Reactions between protons and hydrogen atoms and between hydrogen atoms have many interesting applications especially in the physics of plasmas, and are comparatively simple. The processes

$$p + H \, (1s) \rightarrow p + H(n\ell)$$

and

$$H(1s) + H(1s) \rightarrow H(n'\ell') + H(n\ell) \tag{8-9}$$
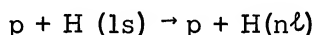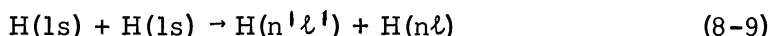
have been studied by Bates and Griffing (1953, 1954, 1955), including the case in which the atom is ionized in the final state. More recently cross sections have been calculated (Pomilla and Milford, 1966) for collisions in which the target and projectile are initially in excited states, including

$$H(1s) + H(n\ell) \rightarrow H(n',\ell') + H(n'',\ell''),$$
$$H(2s) + H(n\ell) \rightarrow H(n',\ell') + H(n'',\ell''). \tag{8-10}$$
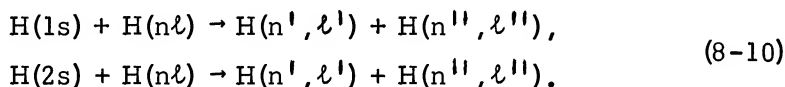
The experiments on atomic hydrogen that exist have been performed at energies that are too low for the Born approximation to be valid, but a detailed comparison with experiment is possible in the case of proton-helium scattering. The excitation of helium to the low lying n^1S, n^1P and n^1D states has been measured[2] (Thomas and Bent, 1967) for incident proton laboratory energies of from 150 kev to 1 Mev. For the same energy rating, Gaillard (1966) has calculated the Born approximation cross sections for excitation to the n^1S states $(n = 4,5,6)$, and to the n^1P $(n = 2,3,4,5)$, n^1D $(n = 3,4,5)$ and 4^1F states. He scaled the earlier calculations of Fox (1966) for excitation by electron impact, using the procedures of Bates and Griffing. The helium ground state wave function was of the form

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[2] These experiments provide cross sections that appear to be inconsistent with those obtained at lower energies by deHeer and his co-workers (deHeer, 1967), but agree with the work of Denis et al (1967) and Robinson and Gilbody (1968).

$$X_0 = R_1\,(r_1)R_2\,(r_2)\,, \tag{8-11}$$

where $R_1\,(r_1)$, $R_2\,(r_2)$ were sums of exponentials, fitted to the Hartree-Fock wave functions. The excited states were of the general form

$$X_n = \psi_n(r_1)\psi_1\,(r_2) + \psi_n(r_2)\psi_1\,(r_1)\,, \tag{8-12}$$

where $\psi_1\,(r)$ was taken to be the wave function of $He^+(1s)$

$$\psi_1 = \sqrt{\frac{8}{\pi}}\ e^{-2r} \tag{8-13}$$
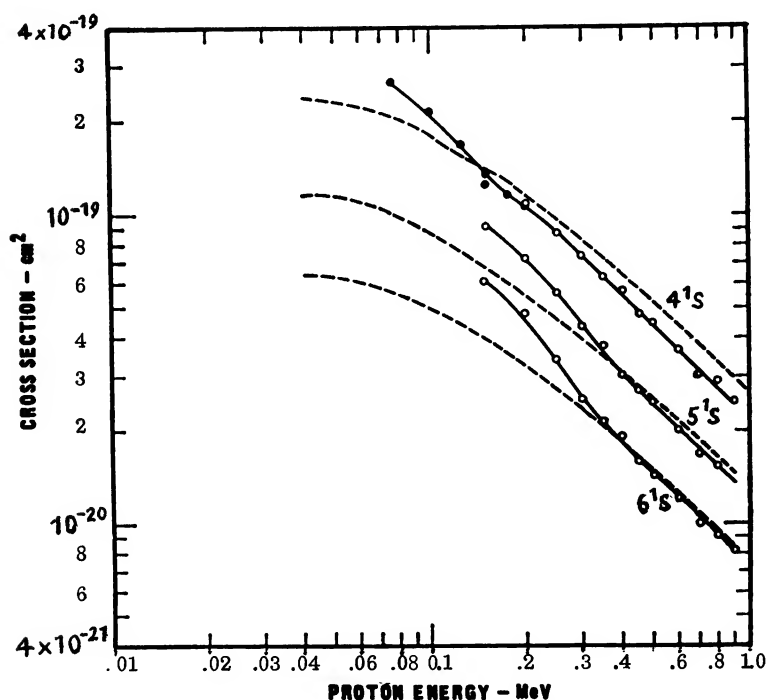
Figure 8-1.   Excitation of helium from the ground state to the n^1S states by deuteron and proton impact.

    o   Proton impact experimental.
    ●   Deuteron impact experimental (Thomas and Bent, 1967).
    ----- Proton impact theoretical Born approximation (Gaillard, 1966).

and $\psi_n(r)$ approximated the wave function of the outer electron moving in the central field of the nucleus screened by the inner electron. This choice of wave function was supported by the agreement of the predicted electron excitation cross section for the transition to 4^1S state with an absolute measurement at 180 ev by Gabriel and Heddle (1960).

The experiments agree closely with the Born cross sections for the final n^1S (n = 4,5,6) states and for the optically allowed transitions to the n^1P states, for energies above 450 kev. This is illustrated in Figure 8-1 for the ^1S states.
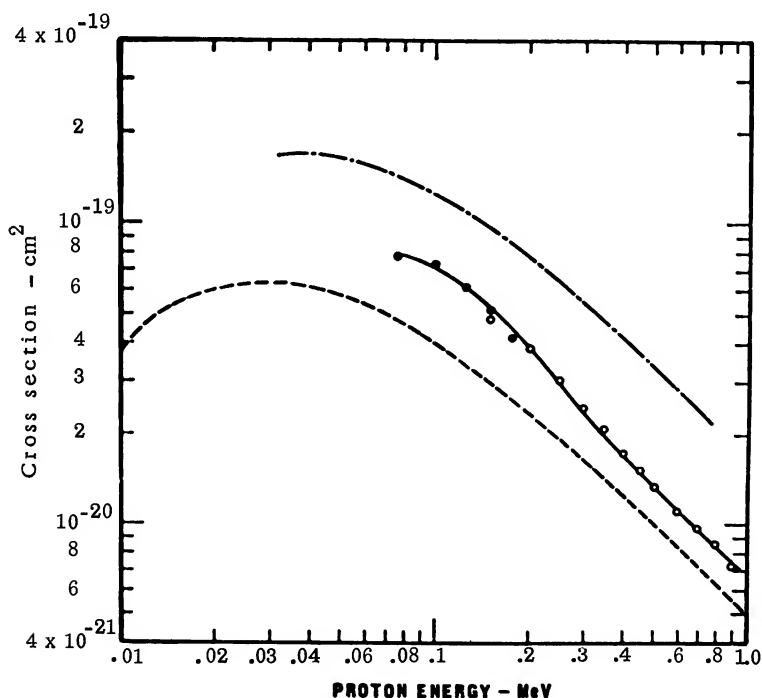
Figure 8-2. Excitation of helium from the ground state to the 4^1D state.

    O   Proton impact experimental.

    ●   Deuteron impact experimental (Thomas and Bent, 1967).

  -----   Theoretical calculations (Born approximation) (Gaillard, 1966).

  -·-·-   Theoretical calculations (Born approximation) (McDowell and Pluta, 1966).

The experiments were also performed with the deuteron rather than the proton as a projectile. If the Born approximation is valid the cross sections should be equal for both projectiles at the same relative velocity. This is well satisfied by the data.

Agreement is less satisfactory for the quadrupole transition to the 4^1D state. In this case, a Born cross section has been computed by McDowell and Pluta (1966), using slightly different wave functions. Their results are appreciably larger than those of Gaillard and the experimental curve falls between the theoretical predictions (see Fig. 8-2). This disagreement reflects the greater sensitivity of the cross section to the wave function as ΔL increases, and it is safe to conclude that the Born approximation[3] should be valid at proton energies above 400 kev, and at corresponding velocities for other projectiles.

Extensive calculations on the inelastic collisions between hydrogen and helium have been carried out by Bates and Crowthers (1967), for the reactions

$$H(1s) + He(1s^2, {}^1S) \rightarrow H(n', \ell') + He(1sn\ell, {}^{1,3}L). \quad (8\text{-}14)$$
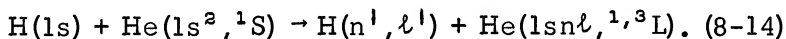
Triplet excitation of helium can only take place through electron exchange, so that wave functions of the correct symmetry must be employed. In a plane wave approximation, the difficulties discussed in connection with the Born-Oppenheimer approximation for electron scattering persist, and Bates and Crowthers adopted Rudge's modification of the Ochkur approximation in their discussion.

Interesting calculations using the impulse approximation have been carried out by Coleman (1968) for excitation of the 2s state of hydrogen by proton impact. In the energy range under consideration (>400 kev), the cross sections agree with those of the Born approximation. At lower energies, the

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[3] In discussing the Born approximation, we have neglected electron exchange. This does not of course occur in proton scattering, but, in atom-atom scattering, although theoretically present, the effect makes a negligible contribution to excitation, except at low velocities, and except for transitions involving a spin change, for example the triplet excitation of helium.

impulse approximation cross sections are smaller than those of
the Born approximation, and may be more accurate, as the Born
approximation invariably overestimates the low energy excita-
tion cross sections, but there is no direct experimental evidence
to assess this work.

Charge exchange

At low energies, the cross sections for charge exchange
reactions can become quite large, but in the high energy region
the charge exchange cross sections are generally much smaller
than those for excitation. This is because the excitation cross
sections decrease like $1/E$ (modified by logarithmic factors
in the case of optically allowed transitions), while the typical
energy variation of the capture cross section is $1/E^6$. We
have already discussed the difficulties in formulating a first
order Born approximation for rearrangement collisions. To see
how these difficulties occur in charge exchange, we shall con-
sider the reaction

$$A + (B + e) \rightarrow (A + e) + B, \qquad (8\text{-}15)$$

where A and B are nuclei of masses M_A, M_B and charges
Z_A, Z_B respectively[4] and e represents the exchanged electron.
The coordinate system that we shall use is shown in Fig. 8-3.
The position vector of the electron e, with respect to the
center of mass of the heavy particles is $\mathbf{r}$, and $\mathbf{R}$ is the posi-
tion vector of B with respect to A. The vectors $(\mathbf{r}, \mathbf{R})$ form a
system of center of mass coordinates. Alternative center of
mass systems are $(\mathbf{r}_A, \mathbf{R}_B)$ where $\mathbf{r}_A$ is the position of the
electron with respect to A and $\mathbf{R}_B$ is the position vector of B
with respect to the center of mass of e and A, and $(\mathbf{r}_B, \mathbf{R}_A)$
where $\mathbf{r}_B$ is the position vector of e with respect to B and
$\mathbf{R}_A$ that of A with respect to the center of mass of e and B.

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[4] In what follows we shall ignore the over-all Coulomb interaction that occurs if both
ions are charged. As explained earlier this effect may be neglected at high energies
and explicit calculations by Bates and Boyd (1962a, b) show that this remains true down
to energies of a few kev.
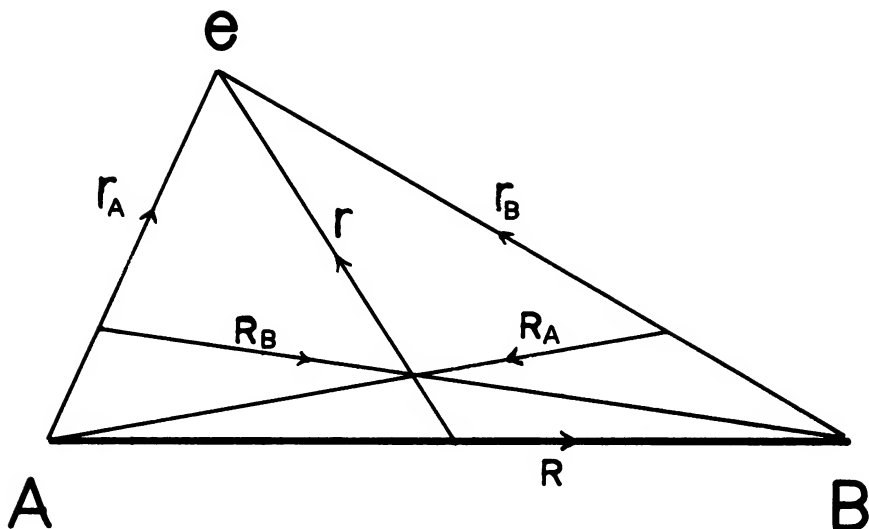
Figure 8-3.   Coordinate system for charge exchange reactions.

The scattering amplitude for charge exchange is then, using atomic units with $e = \hbar = m_e = 1$,

$$g(\theta) = \frac{\mu_f}{2\pi} T_{fi}$$

$$= \frac{\mu_f}{2\pi} \int d\mathbf{r}_A \int d\mathbf{R}_B \left[\psi_{A_f}^* (\mathbf{r}_A) \exp(-i\mathbf{k}_f \cdot \mathbf{R}_B) \right] \left[V_{eB}(\mathbf{r}_B) + \right.$$

$$\left. + V_{AB}(R) \right] \Psi_i^+ (\mathbf{r}_B, \mathbf{R}_A), \qquad (8-16)$$

where μ_f is the reduced mass of B in the final state,

$$\mu_f = \frac{M_B(M_A + 1)}{(M_B + M_A + 1)}. \qquad (8-17)$$

The wave function for the whole system, normalised to an incident plane wave of unit amplitude, is Ψ_i^+ and ψ_{A_f} is the wave function for the atom $(A + e)$ in the final state f.   The

potentials between the electron and the nuclei are V_{eA}, V_{eB},

$$V_{eB}(x) = -\frac{Z_B}{x}, \quad V_{eA}(x) = -\frac{Z_A}{x},$$

while the internuclear potential is

$$V_{AB}(x) = \frac{Z_A Z_B}{x}. \tag{8-18}$$

The angle of scattering θ is the angle between the vector $\mathbf{k}_i$, the center of mass momentum in the initial state of A, and $\mathbf{k}_j$, the center of mass momentum of B in the final state. Conservation of energy requires that

$$\frac{1}{2\mu_A} k_i^2 + \epsilon_i^B = \frac{1}{2\mu_B} k_f^2 + \epsilon_f^A, \tag{8-19}$$

where ϵ_f^A is the binding energy of the atom $(A + e)$ in the final state and ϵ_i^B is that of the atom $(B + e)$ in the initial state. The reduced mass of A in the initial state is defined in a similar way to (8-17). The total cross section for charge exchange is then (atomic units)

$$\sigma_{CE} = 2\pi \int_{-1}^{1} |g(\theta)|^2 \, d\cos\theta, \tag{8-20}$$

where the factor (v_f / v_i), the ratio of the relative velocities in the final and initial states, has been set equal to unity.

Oppenheimer (1928) and Brinkman and Kramers (1930) suggested that the matrix element for $g(\theta)$ could be simplified by ignoring the internucleon potential V_{AB}. They argued that as

$$\mathbf{R}_B = \mathbf{R} + \left(\frac{1}{M_A + 1}\right)\mathbf{r}_A, \tag{8-21}$$

where $M_A \gg 1$, it is permissible to replace $V_{AB}(R)$ by $V_{AB}(R_B)$ to order $(1/M_A)$; but as any potential that is a function of the coordinate joining the center of masses of the colliding aggregates cannot give rise to excitation or rearrangement, it is

expected that the term in V_{AB} can be omitted without appreci-
able error. Kinematically, charge exchange may occur by the
incident particle A picking up an electron while passing the
atom B along an essentially undeflected orbit (because the
mass of the electron is small compared with the mass of A).
Alternatively A and B may change places in a head-on colli-
sion. The probability of this 'knock-on' process is of the
order of $(1/M_A)$ compared with the 'pick-up' process and
vanishes in the limit of infinite nuclear mass. Another way of
looking at this result arises from the semi-classical approxi-
mation. As we pointed out earlier, the heavy particle motion
satisfies the conditions for the semi-classical approximation
to be accurate. Further, at high energies the classical
trajectory is accurately represented by an undeflected straight
line orbit except at very small impact parameters, in which
the collision is head-on. If the heavy particles are undeflected
it follows that the potential between them, V_{AB}, may be ig-
nored, and unless the probability amplitude receives significant
contributions from close collisions, where the impact parameter
$b < 1/M_A$, V_{AB} cannot contribute to the charge exchange ampli-
tude.

Dropping V_{AB} and introducing the unperturbed state for
Ψ_i in (8-16) leads to Brinkman and Kramer's version of the Born
approximation. Although, for the reasons outlined in Chapter
6, it cannot be considered satisfactory (and in practice is not
so), it is interesting to write down the explicit form of the
transition matrix element in this approximation. Setting

$$\Psi_i = \psi_{B_i}(\mathbf{r}_B) \exp(i\mathbf{k}_i \cdot \mathbf{R}_A),$$

and using the relations

$$\mathbf{R}_B = \left(\frac{M_A}{M_A + 1}\right)\mathbf{r}_A - \mathbf{r}_B,$$

$$\mathbf{R}_A = -\mathbf{r}_A + \left(\frac{M_B}{M_B + 1}\right)\mathbf{r}_B,$$

(8-22)

we have that

$$T_{fi} = L(\beta) M(\alpha),\tag{8-23a}$$

where

$$L(\beta) = \int d\mathbf{r}_B \psi_{B_i}(\mathbf{r}_B) V_{eB}(\mathbf{r}_B) \exp(-i\beta \cdot \mathbf{r}_B),\tag{8-23b}$$

$$M(\alpha) = \int d\mathbf{r}_A \psi^*_{A_f}(\mathbf{r}_A) \exp(-i\alpha \cdot \mathbf{r}_A),\tag{8-23c}$$

and

$$\alpha = \mathbf{k}_i + \frac{M_A}{M_A + 1}\mathbf{k}_f,\tag{8-24a}$$

$$\beta = -\mathbf{k}_f - \frac{M_B}{M_B + 1}\mathbf{k}_i.\tag{8-24b}$$

As the momenta $|\mathbf{k}_i|$ and $|\mathbf{k}_f|$ are large, it follows that T_{fi} only receives significant contributions when $\mathbf{k}_i \approx -\mathbf{k}_f$, that is when the incident nucleus A is undeflected. An important point is that it is not a permissible approximation to set

$$\left(\frac{M_A}{M_A + 1}\right) = \left(\frac{M_B}{M_B + 1}\right) = 1$$

in equation (8-24), which is equivalent to ignoring the change in momentum of the electron as it is transferred from B to A. This may be seen by computing the lower limit of $|\alpha|$; if the mass of the electron is ignored this is $\alpha_{min} = 0$. But the correct lower limit to order $(1/M_A)$ is $\alpha_{min} = v^2/4$, where v is the relative velocity of the colliding aggregates, and in view of the exponential character of the integrands in (8-23), this is an all important difference. In contrast, the mass of the electron can be safely ignored when calculating direct excitation cross sections.

Because the capture cross section is peaked about the scattering of the incident nucleus in the forward direction, the capture cross section may be distinguished from the elastic scattering even if the nuclei A and B are identical. For

example in the reactions

$$p + H \rightarrow p + H, \quad (a)$$

and   (8-25)

$$p + H \rightarrow H + p, \quad (b)$$
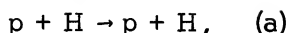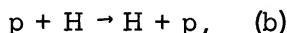
(a) represents elastic scattering and the incident protons are
scattered in the forward direction in the center of mass system
and the hydrogen atoms appear in the backward direction. In
the charge exchange reaction (b), the incident protons, which
have now captured an electron and appear as hydrogen atoms,
are scattered again in the forward direction. The peaks in the
forward and backward directions are well separated and a
distinct charge exchange cross section can be measured. This
statement must be qualified at very low energies and also at
very high energies, as we shall see. The Brinkman-Kramers
cross section for electron capture into the hydrogen-atom ground
state is easily evaluated. In this case

$$\alpha^2 = \beta^2 \doteq \frac{v^2}{4}\left(1 + 4M^2 \sin^2(\theta/2)\right) \qquad (8\text{-}26a)$$

and

$$T_{fi} \doteq -\frac{32\pi}{(1 + \alpha^2)^3}, \qquad (8\text{-}26b)$$

where M is the mass of the proton. The cross section becomes

$$\sigma_{B.K.} = \frac{2^8}{5(1 + v^2/4)^5 v^2}, \qquad (8\text{-}27)$$

which exhibits the characteristic $(1/v^{12})$ variation at high
energies.

Cross sections for a number of reactions have been
calculated in this approximation, and over the energy range of
interest (1 - 1,000 kev) are quite inadequate (Bransden, 1965),
exceeding the measured cross section by a large margin (see
Fig. 8-4).

As a result of this disagreement, calculations have
been carried out in the Born approximation, retaining the inter-
nuclear potential V_{AB}, in the hope that the error in estimating
the matrix element V_{AB} will cancel that in the Brinkman-
Kramers matrix element. In fact, the cross sections found in
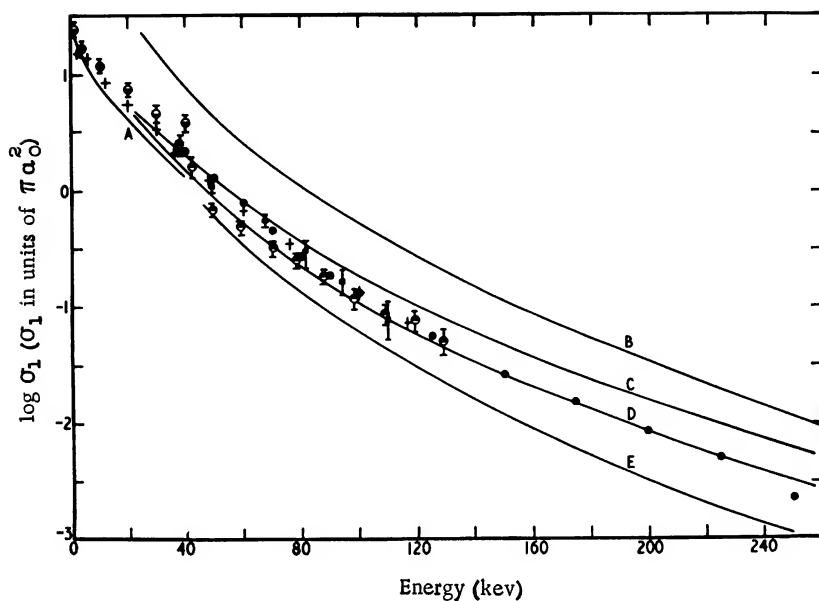
Figure 8-4.   Total charge exchange cross section for protons in atomic hydrogen.
Experimental results: —

        ●   Whitthower et al. (1966).
        ◑   Fite et al. (1962).
        ◔   Gilbody and Ryding (1966).
        +   McClure (1966).

Theoretical calculations: —

      A   Two-state molecular expansion (Ferguson, 1961).
      B   Brinkman and Kramers approximation.
      C   Two-state atomic expansion (McCarrol, 1961; McElroy, 1963).
      D   Born approximation (Jackson and Schiff, 1953; Bates and Dalgano, 1952; Mapleton, 1962).
      E   Impulse approximation (Coleman and McDowell, 1965).

this way do agree with the measured cross sections by electron capture by protons from hydrogen atoms[5] and from helium atoms[6] quite well (see Figs. 8-4 and 8-5), although at the higher energies there is some suggestion that the Born cross
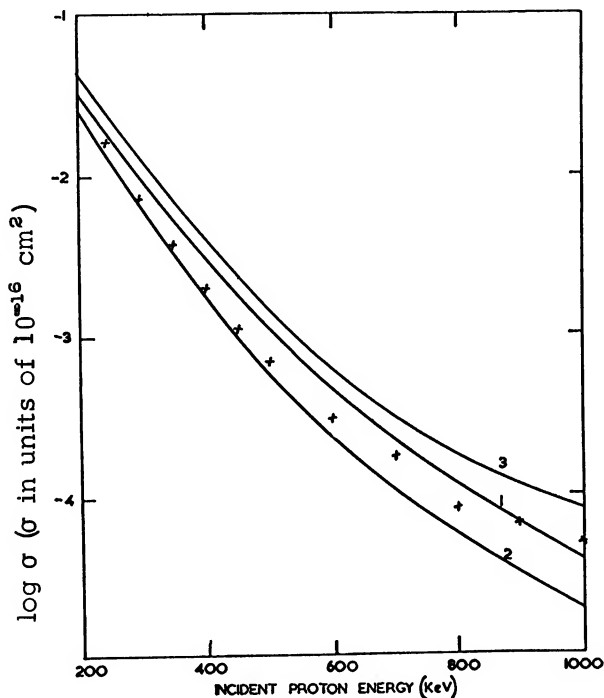
Figure 8-5.   Total charge exchange cross section for protons in helium.
Experimental results: x (Stier and Barnett, 1956; Barnett and Reynolds, 1958).
Theoretical calculations: —

        1.   Born approximation (Mapleton, 1961).
        2.   Impulse approximation (Bransden and Cheshire, 1963).
        3.   Atomic eigenfunction expansion (Sin Fai Lam, 1967).

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[5] Jackson and Schiff (1953); Bates and Dalgano (1952).

[6] Mapleton (1961, 1963a).

section is too small. The high energy limit of the Born approximation is

$$\sigma_B \rightarrow 0.661 \, \sigma_{B.K.}$$

An exception is the case of symmetrical resonance in which the nuclei A and B are identical. In that case σ_B is ultimately proportional to $1/v^6$. This is because, when the nuclei A and B are identical, the "knock-on" process, in which incident nucleus A exchanges with the target nucleus B, becomes the dominant process at extremely high energies (>80 Mev)[7]. These asymptotic forms are reached only at energies beyond the region of experimental interest at present (>10-40 Mev).

   Because of the difficulties with the theoretical foundations of the Born approximation, it is likely that the apparent agreement with the cross section is accidental. Some of these difficulties do not occur in the first order exchange approximation that was discussed in Chapter 6. As before, this may be derived from a two state approximation, or from a distorted wave formulation and takes the form (Basel and Gerguoy, 1960; Bates, 1958; Takayanagi, 1955)

$$T_{fi} = \int d\mathbf{r}_A \int d\mathbf{R}_B \psi_{A_f}^*(\mathbf{r}_A) \exp(-i\mathbf{k}_f \cdot \mathbf{R}_B)\left[V_{eB}(\mathbf{r}_B) + \right.$$

$$\left. + V_{AB}(R) - \bar{V}(\mathbf{r}_B)\right]\psi_{B_i}(\mathbf{r}_B) \exp(i\mathbf{k}_i \cdot \mathbf{R}_A) \quad (8\text{-}28)$$

where $\bar{V}$ is the average interaction in the final state

$$\bar{V}(\mathbf{R}_B) = \int d\mathbf{r}_A |\psi_{A_f}(\mathbf{r}_2)|^2 \left(V_{eB}(\mathbf{r}_B) + V_{AB}(R)\right). \qquad (8\text{-}29)$$

The satisfactory features of this approximation are that, to order $(1/M_A)$, T_{fi} becomes completely independent of the internuclear potential V_{AB} and that asymptotically the cross section σ_{BG} tends to the Brinkman-Kramers result. Numerical calculation shows that making an allowance for the non-orthogonality of the incident and final states in this way is effective in reducing the cross section over the energy range 250 kev - 1 Mev from the Brinkman-Kramers values to values

[7]Mapleton (1964a).

comparable with, but slightly exceeding those of the Born app-
roximation. Although the total cross sections σ_B and σ_{BG}
are quite close, the angular distributions are different in
detail (see Bransden, 1965), but in both cases the scattering
is peaked about the forward direction (for nucleus A) so that
no experimental distinction on this count is possible.

    Although σ_B and σ_{BG} are of the same order of magni-
tude as the experimental results, agreement is not perfect and
there are further theoretical indications that the approximations
are inadequate. Calculation (Drisko, 1955; Mapleton, 1967)
indicates that the contribution of the second Born approximation
ultimately ($\gg 10$ Mev) exceeds that of the first Born approxima-
tion. This might be dismissed as an indication of the lack of
convergence of the Born series (see Chapter 6), but calcula-
tions based on the impulse approximation provide a cross
section σ_I that does not tend to the Brinkman-Kramers cross
section but behaves in a similar way to the second Born
approximation. For electron capture by protons in hydrogen

$$\sigma_I \sim \left(0.2946 + \frac{5\pi v}{2^{11}}\right)\sigma_{B.K.} \qquad (8\text{-}30)$$

In both cases, the modification of the first order matrix elements
arises from intermediate states corresponding to a double scat-
tering of the electron by the two nuclei, each scattering being
sharply peaked about 60° in the laboratory frame of reference.
Unlike the first order matrix elements, which at high energies
are derived from the high momentum components of one of the
bound state wave functions, the double scattering term is
derived primarily from the low momentum components of both
bound state wave functions. There is an interesting classical
analogue to the capture process, discussed by Thomas (1927).
In this, capture is pictured classically as two successive two-
body Rutherford scatterings. In the first, the electron is
scattered by the incident proton toward the target proton and
acquires the velocity of the incident proton, which continues
to move on its original path. Conservation of energy and mo-
mentum then requires the angle of scattering to be 60° in the
laboratory frame. In the second collision (between the electron
and the target proton), the speed of the electron is unaltered,
but it is deflected so that it moves parallel to the incident
proton. The velocity dependence of the process is as for the

second Born approximation.

These factors suggest that continuum intermediate states may be important in the capture problem and that first order methods will fail at very high energies, and possibly even in the experimental region, say 250 kev – 1 Mev, there may be important contributions from higher order terms.

Cross sections in the impulse approximation, for electron capture by protons in hydrogen (Coleman and McDowell, 1965; Coleman and Trelease, 1967) and for protons in helium (Bransden and Cheshire, 1963) fall below the experimental measurements (see Figs. 8-4, 8-5), and do not seem to be satisfactory. The classical model of Thomas has been refined by Bates et al. (1964) and Bates and Mapleton (1966) and has been used to discuss certain ion-molecule collisions with some success.

8-2   THE SEMI-CLASSICAL APPROXIMATION IN ION-ATOM SCATTERING

In the previous paragraph, we saw that the first order Born approximation is quite successful in describing excitation at incident energies greater than several hundred kev. It is possible to attempt to calculate the second Born approximation,[8] but this is a task of major difficulty, and the energies for which such an approximation is valid are usually not so far below the domain of the velocity of the first Born approximation, to make the attempt worthwhile. As in electron scattering, by introducing a parameter that cuts off the matrix element for small impact parameters, the range of validity of the Born approximation can be extended, but this is essentially an arbitrary procedure and although useful semi-empirical results can be obtained, we shall not discuss them here.

To extend the theory to low energies it is natural to attempt to use expansion methods similar to the close coupling method that was described in connection with electron scattering. There is no difficulty in writing down coupled equations obtained by expanding the wave function for the system in the

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[8]For work on the second Born approximation see Bates (1962).

complete set of target and projectile eigenfunctions. Equations for the radial wave functions are found by making the usual decomposition into angular momentum states. Because large values of the angular momentum are important, the W.K.B. method is used to solve these equations. An alternative procedure, which we shall follow, is to introduce the semi-classical approximation for the nuclear motion at an earlier stage.[9]

Let us again consider a system in which a nucleus A is incident on an atom composed of one electron bound to nucleus B, and take coordinates shown in Fig. 8-3, where $\mathbf{R}_A$ and $\mathbf{R}_B$ are the vectors joining A and B to the center of mass of (B + e) and (+ e) respectively. As $\mathbf{R}$, the internuclear distance, and $\mathbf{r}$, the coordinate joining the electron to the center of mass of A and B, form a center of mass system of coordinates, the Schrödinger equation in that system is

$$(H - E)\Psi = \left[-\frac{\hbar^2}{2\mu}\nabla_R^2 - \frac{\hbar^2}{2m}\nabla_r^2 + V_{Ae} + V_{Be} + V_{AB} - E\right]\Psi(\mathbf{R},\mathbf{r})$$

$$= 0, \qquad\qquad (8\text{-}31)$$

where μ is the reduced mass of A and B and m is the mass of the electron

$$\mu = \frac{M_A M_B}{M_A + M_B}. \qquad\qquad (8\text{-}32)$$

The boundary conditions to be satisfied by Ψ are that, for large $|\mathbf{R}_A|$,

$$\Psi(\mathbf{r},\mathbf{R}) \xrightarrow[R_A \to \infty]{} \sum_n \left[\delta_{n0}\, e^{i\mathbf{k}_0 \cdot \mathbf{R}_A} + f_{no}(\theta_A)\frac{e^{ik_n R_A}}{R_A}\right]\psi_{B_n}(\mathbf{r}_B)$$

$$(8\text{-}33)$$

where $f_{no}(\theta)$ is the scattering amplitude corresponding to excitation of the nth state of the target atom, with

---

[9] In this section the methods of Bates and Holt (1966) and Bates and McCarroll (1958) are followed.

eigenfunction $\psi_{B_n}(\mathbf{r}_B)$. As rearrangement collisions are also possible, in which the electron is captured by nucleus A, we must also have for large R_B

$$\Psi(\mathbf{r}, \mathbf{R}) \xrightarrow[R_B \to \infty]{} \sum_m g_{mo}(\theta_B) \frac{e^{iK_m R_B}}{R_B} \psi_{A_m}(\mathbf{r}_A), \qquad (8-34)$$

where $g_{mo}(\theta)$ is the cross section for capture into the mth state of the atom A with eigenfunction $\psi_{A_m}(\mathbf{r}_A)$. In these equations $\hbar k_n$ and $\hbar K_m$ are, in our usual notation, the center of mass momenta in channels n and m.

We shall now expand $\Psi(\mathbf{r}, \mathbf{R})$ in the form

$$\Psi(\mathbf{r}, \mathbf{R}) = \left[\sum_n F_n(\mathbf{R})\chi_n(\mathbf{r}, \mathbf{R}) + \sum_m G_m(\mathbf{R})\varphi_m(\mathbf{r}, \mathbf{R}) \right], \quad (8-35)$$

where F_n and G_m are defined so that as $R \to \infty$

$$F_n(\mathbf{R}) \sim \delta_{no} \exp\left[i\mathbf{k}_o \cdot \mathbf{R}\right] + f_{no}(\Theta_R) \, e^{ik_n R}/R$$

$$G_m(\mathbf{R}) \sim g_{mo}(\pi - \Theta_R) \, e^{ikR}/R. \qquad (8-36)$$

The functions χ_m and φ_m are then chosen so that asymptotically each term in the expansion corresponds to one term in the sums (8-33) and (8-34). This requires that

$$\chi_n(\mathbf{r}, \mathbf{R}) \xrightarrow[R \to \infty]{} \psi_{B_n}(\mathbf{r}_B) \exp\left(i\ell_1 \mathbf{k}_n \cdot \mathbf{r}_B\right) \qquad (8-37)$$

$$\varphi_m(\mathbf{r}, \mathbf{R}) \xrightarrow[R \to \infty]{} \psi_{A_m}(\mathbf{r}_A) \exp\left(i\ell_2 \mathbf{k}_m \cdot \mathbf{r}_A\right), \qquad (8-38)$$

where

$$\ell_1 = -\left(\frac{m}{M_B + m}\right) \qquad (8-39a)$$

$$\ell_2 = +\left(\frac{m}{M_A + m}\right). \qquad (8-39b)$$

The exponential factors are required to correct for the fact that
$\mathbf{R}$ does not coincide with either of the center of mass vectors
$\mathbf{R}_A$ or $\mathbf{R}_B$, in terms of which the asymptotic conditions are de-
fined. The symmetrical phase factors do not alter the calcula-
tion of fluxes so that the cross sections are determined by
$|f_{no}|^2$ and $|g_{mo}|^2$ in the usual way.

The asymptotic forms do not define φ_m or χ_n com-
pletely and, as we shall see, a good deal of freedom remains
in their choice. From the variational method, F_n and G_m can
be determined from the coupled equations

$$(\chi_n, (H - E)\Psi) = 0, \quad n = 0, 1, \ldots,$$

$$(\varphi_m, (H - E)\Psi) = 0, \quad m = 0, 1, \ldots. \tag{8-40}$$

Without loss of generality, we can take the energy independent
functions $\chi_n(\mathbf{r}, \mathbf{R})$ to form an orthonormal set at each value of
$\mathbf{R}$

$$(\chi_n, \chi_m) = \delta_{nm} \tag{8-41}$$

and similarly for the functions φ_n

$$(\varphi_m, \varphi_n) = \delta_{mn}. \tag{8-42}$$

It is clear that asymptotically the functions φ_m are orthogonal
to the functions χ_n. It is possible to construct the functions
so that the φ_m and χ_n are orthogonal for all values of $\mathbf{R}$, but,
except in a two state approximation, this is difficult to achieve
in practice and we will not assume orthogonality in what fol-
lows. To reduce the set of equations (8-40) we first decompose
H into

$$H = \bar{H} - \frac{\hbar^2}{2\mu} \nabla_R^2, \tag{8-43}$$

where

$$\bar{H} = -\frac{\hbar^2}{2m} \nabla_r^2 + V_{Ae} + V_{Be} + V_{AB}.$$

The first set of equations (8-40) then becomes

$$\sum_m \left(X_n , \left(\frac{\hbar^2}{2\mu} \nabla_R^2 + \frac{\hbar^2}{2\mu} k_m^2 \right) X_m \ F_m \right) = \sum_m V_{nm} \ F_m -$$

$$- \sum_m \left(X_n , \left(\frac{\hbar^2}{2\mu} \nabla_R^2 + \frac{\hbar^2}{2\mu} K_m^2 \right) \varphi_m G_m \right) + \sum_m H_{nm} G_m ,$$

where $\hspace{9cm}$ (8-44)

$$V_{nm} = \left(X_n , \left(\bar{H} - \epsilon_m^B \right) X_m \right),$$ $\hspace{3cm}$ (8-45a)

$$H_{nm} = \left(X_n , \left(\bar{H} - \epsilon_m^A \right) \varphi_m \right),$$ $\hspace{3cm}$ (8-45b)

and the second set is similar in form,

$$\sum_n \left(\varphi_m , \left(\frac{\hbar^2}{2\mu} \nabla_R^2 + \frac{\hbar^2}{2\mu} K_n^2 \right) \varphi_n \ G_n \right) = \sum_n U_{mn} \ G_n -$$

$$- \sum_n \left(\varphi_m , \left(\frac{\hbar^2}{2\mu} \nabla_R^2 + \frac{\hbar^2}{2\mu} k_n^2 \right) X_n F_n \right) + \sum_n T_{mn} F_n \quad (8-46)$$

where

$$U_{mn} = \left(\varphi_m , \left(\bar{H} - \epsilon_n^A \right) \varphi_n \right),$$ $\hspace{3cm}$ (8-47a)

and

$$T_{mn} = \left(\varphi_m , \left(\bar{H} - \epsilon_n^B \right) X_n \right).$$ $\hspace{3cm}$ (8-47b)

As X_m and φ_m depend on **R** as well as **r**, we have that

$$\frac{\hbar^2}{2\mu} \nabla_R^2 \left\{ X_n(\mathbf{r},\mathbf{R}) F_n(\mathbf{R}) \right\} = \frac{\hbar^2}{2\mu} \left\{ F_n(\mathbf{R}) \nabla_R^2 X_n(\mathbf{r},\mathbf{R}) + \right.$$

$$\left. + 2 \boldsymbol{\nabla}_R X_n(\mathbf{r},\mathbf{R}) \cdot \boldsymbol{\nabla}_R F_n(\mathbf{R}) + X_n(\mathbf{r},\mathbf{R}) \nabla_R^2 F_n(\mathbf{R}) \right\}.$$

However the functions $X(\mathbf{r},\mathbf{R})$ vary slowly with **R** (as may be seen from their asymptotic form) compared with the variation of $F_n(\mathbf{R})$ with **R** (which depends on the large wave number k_n), so that the term $\nabla_R^2 X_n$ may be neglected,[10] and the same is true for $\nabla_R^2 \varphi_m$. Using the orthonormal properties of the X_m, the

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[10] The small terms $\hbar^2/2\mu (X_n , \nabla_R^2 X_m)$ and $\hbar^2/2\mu (X_n , \nabla_R^2 \varphi_m)$ could be included in the definition of V_{nm} and H_{nm} if it is desired to retain them.

first set of equations can be written as

$$\left(\frac{\hbar^2}{2\mu}\nabla_R^2 + \frac{\hbar^2}{2\mu}k_n^2 - V_{nn}\right) F_n(\mathbf{R}) = \sum_{m \neq n} V_{nm}F_m(\mathbf{R}) - $$

$$- \sum_m \left[\mathbf{\gamma}_{nm} \cdot \nabla_R F_m(\mathbf{R}) + S_{nm}\left(\frac{\hbar^2}{2\mu}\nabla_R^2 + \frac{\hbar^2}{2\mu}K_m^2\right) G_m(\mathbf{R}) + \right.$$

$$\left. + \mathbf{\Gamma}_{nm} \cdot \nabla_R G_m(\mathbf{R}) - H_{nm}G_m(\mathbf{R})\right], \quad (8\text{-}49)$$

where

$$S_{nm} = (\chi_n, \varphi_m),$$

$$\mathbf{\gamma}_{nm} = 2(\chi_n, \nabla_R \chi_m) \quad \mathbf{\Gamma}_{nm} = 2(\chi_n, \nabla_R \varphi_m), \quad (8\text{-}50)$$

The second set of equations is

$$\left(\frac{\hbar^2}{2\mu}\nabla_R^2 + \frac{\hbar^2}{2\mu}K_m^2 - U_{mm}\right) G_m(\mathbf{R}) = \sum_{n \neq m} U_{mn}G_n(\mathbf{R}) - $$

$$- \sum_n \left[\mathbf{\Delta}_{mn} \cdot \nabla_R G_n(\mathbf{R}) + (S^\dagger)_{mn}\left(\frac{\hbar^2}{2\mu}\nabla_R^2 + \frac{\hbar^2}{2\mu}k_n^2\right) F_n(\mathbf{R}) + \right.$$

$$\left. + (\mathbf{\Gamma}^\dagger)_{mn} \cdot \nabla_R F_n(\mathbf{R}) - T_{mn}F_n(\mathbf{R})\right], \quad (8\text{-}51)$$

where $\mathbf{\Delta}_{mn} = 2(\varphi_m, \nabla_R \varphi_n)$. These equations, apart from omission of the terms in $\nabla_R^2 \chi_n$ and $\nabla_R^2 \varphi_m$, are exact. Next the functions F_n and G_m are written in product form:—

$$F_n(\mathbf{R}) = \mathfrak{F}_n(\mathbf{R})A_n(\mathbf{R})$$

$$G_m(\mathbf{R}) = \mathfrak{G}_m(\mathbf{R})C_m(\mathbf{R}), \quad (8\text{-}52)$$

where $\mathfrak{F}_n(\mathbf{R})$ and $\mathfrak{G}_m(\mathbf{R})$ are the solutions of the equations in the absence of coupling between the states χ_n or φ_m.

$$\left(\frac{\hbar^2}{2\mu}\nabla_R^2 + \frac{\hbar^2}{2\mu}k_n^2 - V_{nn}(R)\right)\mathfrak{F}_n(\mathbf{R}) = 0,$$

$$\left(\frac{\hbar^2}{2\mu}\nabla_R^2 + \frac{\hbar^2}{2\mu}K_m^2 - U_{mm}(R)\right)\mathfrak{G}_m(\mathbf{R}) = 0. \quad (8\text{-}53)$$

The solutions of these equations, in the interaction region, can be represented accurately by the semi-classical approximations discussed in Chapter 2. In the lowest order approximation, the eikonal approximation, we have that (see equations (2-94), (1-96) and (2-99))

$$\mathfrak{I}_n(\mathbf{R}) = \exp{(iS_n(\mathbf{b}, Z))},$$

$$\mathfrak{G}_m(\mathbf{R}) = \exp{(i\mathfrak{s}_m(\mathbf{b}, Z))},$$

$$(8\text{-}54)$$

where

$$S_n(\mathbf{b}, Z) = k_n Z + \int_{-\infty}^{Z} \left\{ \left[k_n^2 - \frac{2\mu}{\hbar^2} V_{nn} \right]^{1/2} - k_n \right\} dZ,$$

$$(8\text{-}55)$$

$$\mathfrak{s}_m(\mathbf{b}, Z) = K_m Z + \int_{-\infty}^{Z} \left\{ \left[K_m^2 - \frac{2\mu}{\hbar^2} U_{mm} \right]^{1/2} - K_m \right\} dZ.$$

The integration is carried out over a classical straight line trajectory

$$\mathbf{R} = \mathbf{b} + \hat{\mathbf{n}} Z,$$
$$(8\text{-}56)$$

where $\hat{\mathbf{n}}$ is a unit vector in the direction of incidence and $\mathbf{b} \cdot \hat{\mathbf{n}} = 0$. It is important to remember that although the interaction is ignored in the trajectory, the functions $\mathfrak{s}_m$ and S_n contain sufficient phase information to describe various non-classical interference effects correctly. At sufficiently low energies, the approximation of a straight line trajectory breaks down. In this case, the integrals occurring in S_n and $\mathfrak{s}_m$ should be replaced by integrals over the correct classical trajectory. For collisions in which either the projectile or target is neutral, straight line trajectories may be used down to energies of a few hundred electron volts or even less. Where both the projectile and the target are charged, the diagonal interactions V_{nn} will be asymptotic to a Coulomb interaction, and it is necessary to use the corresponding Coulomb trajectory at energies below a few thousand electron volts. Some examples have been discussed by Bates and Boyd (1962a,b).

From (8-52), using the eikonal approximations (8-55) we have that

$$\nabla_R^2 F_n(\mathbf{R}) \simeq \mathfrak{F}_n(\mathbf{R}) \frac{\partial^2}{\partial Z^2} A_n(\mathbf{b}, Z) + 2i p_n \mathfrak{F}_n(\mathbf{R}) \frac{\partial}{\partial Z} A_n(\mathbf{b}, Z) -$$

$$- p_n^2 \mathfrak{F}_n(\mathbf{R}) A_n(\mathbf{b}, Z)$$

$$(8-57)$$

$$\nabla_R^2 G_m(\mathbf{R}) \simeq \mathfrak{G}_m(\mathbf{R}) \frac{\partial^2}{\partial Z^2} C_m(\mathbf{b}, Z) + 2i q_m \mathfrak{G}_m(\mathbf{R}) \frac{\partial}{\partial Z} C_n(\mathbf{b}, Z) -$$

$$- q_m^2 \mathfrak{G}_m(\mathbf{R}) C_n(\mathbf{b}, Z),$$

where

$$p_n^2 = \left[k_n^2 - \frac{2\mu}{\hbar^2} V_{nn} \right], \quad q_m^2 = \left[K_m^2 - \frac{2\mu}{\hbar^2} U_{mm} \right]. \quad (8-58)$$

The major approximation (other than that of straight line trajectories) is to neglect $\partial^2 A_n/dZ^2$ and $\partial^2 C_m/\partial Z^2$ in comparison with $\partial A_n/\partial Z$ or $\partial C_m/\partial Z$. At very low energies, this condition may not always be satisfied in the interaction region. In this case systematic correction procedures based on the omitted term can be devised and such correction procedures (based on a slightly different form of the equations) have been discussed by Wilets and Wallace (1968).

In the coupled equations (8-49) and (8-51), terms in ∇F_n or ∇G_m appear on the right hand side, and to a sufficient approximation we have that

$$p_n \gg \frac{\partial A_n}{\partial Z}, \quad q_m \gg \frac{\partial C_m}{\partial Z}$$

so that

$$\nabla F_n \simeq i p_n F_n \hat{\mathbf{n}}$$

$$(8-59)$$

$$\nabla G_m \simeq i q_m G_m \hat{\mathbf{n}}.$$

With these approximations, the final form of the coupled equations (8-49) and (8-51) is

$$2i \left(\frac{\hbar^2}{2\mu} \right) p_n \frac{\partial A_n}{\partial Z} = \sum_m \left[V_{nm} (1 - \delta_{nm}) - i p_m \, \mathbf{\gamma}_{nm} \cdot \hat{\mathbf{n}} \right] \times$$

$$\times A_m \exp\left[i (S_m - S_n) \right] - \sum_m \left[2i \left(\frac{\hbar^2}{2\mu} \right) S_{nm} q_m \frac{\partial C_m}{\partial Z} + \right.$$

$$+ \left\{ S_{nm} U_{mm} + \mathbf{\Gamma}_{nm} \cdot \hat{\mathbf{n}} \right) - H_{nm} \right\} C_m \Bigg] \exp[i(S_m - S_n)].$$

$$(8\text{-}60a)$$

$$2i \left(\frac{\hbar^2}{2\mu} \right) q_m \frac{\partial C_m}{\partial Z} = \sum_n \left[U_{mn} (1 - \delta_{mn}) - iq_n \mathbf{A}_{mn} \cdot \hat{\mathbf{n}} \right] \times$$

$$\times C_n \exp[i(S_n - S_m)] - \sum_n \left[2i \left(\frac{\hbar^2}{2\mu} \right) (S^\dagger)_{mn} p_n \frac{\partial A_n}{\partial Z} + \right.$$

$$+ \left\{ (S^\dagger)_{mn} V_{nn} + (\mathbf{\Gamma}^\dagger)_{mn} \cdot \hat{\mathbf{n}} - T_{mn} \right\} A_n \exp \Bigg] [i(S_n - S_m)].$$

$$(8\text{-}60b)$$

Although these equations have a somewhat complicated appearance, they are only of first order in $\partial/\partial Z$ and are less complicated in structure than the integral-differential equations of the usual close coupling method, discussed in Chapters 5 and 6. The boundary conditions follow by requiring that the system initially describes the situation in which the nucleus A is free and the electron is bound to B in the ground state. This requires that as $Z \to -\infty$

$$A_0 \to 1$$

and

$$A_n \to 0, \quad n \neq 0$$

$$C_m \to 0, \quad \text{all } m.$$

The cross section for excitation of the nth state of the atom (B + e) is determined by the value of $\underset{Z \to +\infty}{\ell t} \; A(\mathbf{b}, Z) = A(\mathbf{b}, \infty)$

$$\sigma_{no} = 2\pi \left(\frac{k_n}{k_0} \right) \int_0^\infty b \, db \, |A_n(b, \infty)|^2 \qquad (8\text{-}61)$$

while that for charge exchange in which the electron is captured into the mth state of the atom (A + e) is

$$\sigma_{mo}^{CE} = 2\pi \left(\frac{K_m}{k_0} \right) \int_0^\infty b \, db \, |C_m(b, \infty)|^2. \qquad (8\text{-}62)$$

So far it has been assumed that the nuclei A and B are distinct,

but the case of symmetrical resonance, when A is identical
with B, is of great importance and the modifications introduced
to cover this case will be dealt with later. The formulae may
be modified to cover the case in which the assumption of a
straight line trajectory is invalid, by (Bates and Holt, 1966)

(a) in the definitions of S_m and S_n replacing $\int dZ$ by $\int d\mathbf{s}$
     where $d\mathbf{s}$ is an element of length along the trajectory;
(b) replacing $\partial/\partial Z$ where it occurs by $\partial/\partial s$, differentia-
     tion along the trajectory; and
(c) replacing $\hat{\mathbf{n}}$ the unit vector in the direction of incidence
     by a unit vector $\hat{\mathbf{n}}(s)$ parallel to the trajectory.

It is assumed that the classical trajectories in all the channels
are the same to a sufficient approximation, although the phases
are of course different. The question of the angular distribu-
tions, and the interference effects that arise in certain cases
when this assumption is incorrect, will be dealt with later.

The impact parameter method

Provided the velocity of impact is not too small, the
difference in the relative velocity of the heavy particles in
each channel may be ignored. We can then set

$$Z = vt,$$

where $t = 0$ corresponds to the time of closest approach and
v is the relative velocity of the heavy particles. Then where
q_m and p_n occur in the coefficients of the equations (8-60),
we can make the approximations

$$\frac{\hbar q_m}{\mu} = \frac{\hbar p_m}{\mu} = v. \tag{8-63}$$

The exponentials containing S_m and S_m may also be simpli-
fied. Expanding the square roots in (8-55) for
$k_n^2 \gg 2\mu/\hbar^2 \, V_{nn}$, $K_m^2 \gg 2\mu/\hbar^2 \, U_{mm}$ and making the approxima-
tion (cf. 8-5)

$$(k_n - k_m) \approx \left(\frac{\epsilon_m^B - \epsilon_n^B}{\hbar v} \right),$$

we obtain the result:—

$$S_m - S_n \simeq \left[\frac{1}{\hbar v} \int_{-\infty}^{Z} [V_{nn} - V_{mm}] dZ + \left(\frac{\epsilon_n^B - \epsilon_m^B}{\hbar v} \right) Z \right] (8\text{-}64)$$

Similar results can be obtained for $(S_m - S_n)$ and $(S_m - S_n)$. The coupled equations are then identifiable with those obtained from the time dependent Schrödinger equation

$$\left(\overline{H}(t) - i\hbar \frac{\partial}{\partial t} \right) \Psi(\mathbf{r}, t) = 0, \tag{8-65}$$

where $\overline{H}$ is defined as before and depends on t, through the relationship $\mathbf{R} = \mathbf{b} + \mathbf{v}t$, $\mathbf{b} \cdot \mathbf{v} = 0$. If Ψ is expanded according to

$$\Psi(\mathbf{r}, t) = \sum_n A_n(\mathbf{b}, t) \chi_n(\mathbf{r}, \mathbf{R}) e^{-i \left(\epsilon_n^B + mv^2/2 \right) t} +$$

$$+ \sum C_m(\mathbf{b}, t) \varphi_m(\mathbf{r}, \mathbf{R}) e^{-i \left(\epsilon_m^A + mv^2/2 \right) t}, \tag{8-66}$$

we find that A_n and C_m satisfy equations (8-60) in the simplified form. In this form, the approximation is known as the impact parameter approximation.

Choice of χ_n, φ_m

The functions χ_n and φ_m have been specified in terms of the asymptotic forms (8-38, 8-39) with certain orthogonality and normality conditions. The construction of suitable sets of functions must be guided by physical considerations with the aim of providing an accurate representation of the wave function when the set of functions χ_n or φ_m is truncated to a few terms leading to equations of manageable size for computation. At very low energies, where nearly adiabatic conditions apply, to a first approximation the kinetic energy of the heavy particles can be neglected. For each fixed distance $\mathbf{R}$, the Schrödinger equation of this two center problem may be solved

$$\overline{H}(\mathbf{r}, \mathbf{R}) \psi_n(\mathbf{r}, \mathbf{R}) = \eta_n(R) \psi_n(\mathbf{r}, \mathbf{R}), \tag{8-67}$$

to provide a set of molecular wave functions ψ_n. The functions χ_n or φ_m may then be chosen to be those combinations of the

molecular orbitals ψ_n that satisfy the boundary conditions. This expansion in terms of molecular wave functions is called the perturbed stationary state method (Massey and Smith, 1933) and is similar to the polarized orbital method described earlier.

When the relative velocity of the nuclei A and B becomes comparable with the electronic velocity, the wave function cannot be expected to adjust adiabatically so that at each instant it coincides approximately with the molecular function. In this situation, the electron will be associated for most of the time with one or other of the nuclei and this situation can be represented by taking χ_n and φ_m to be atomic wave functions. That is χ_n and φ_m are identified with their asymptotic forms. With either choice, the sets of functions χ_n, φ_m are complete.

The quantities $\mathbf{\gamma}_{nm} \cdot \hat{\mathbf{n}}$, $\mathbf{\Gamma}_{nm} \cdot \hat{\mathbf{n}}$, $\Delta_{nm} \cdot \hat{\mathbf{n}}$ are the matrix elements of the operator $\partial/\partial Z$, where Z is the component of $\mathbf{R}$ in the direction of incidence, with respect to the functions χ_n and φ_m. If these functions are spherically symmetric, all these quantities vanish, but in all other cases these matrix elements will be non-zero and generally of importance. In taking the derivatives of χ_n and φ_m with respect to Z, it is important to specify the axis of quantization carefully. Usually molecular wave functions are specified by taking the internuclear axis as the axis of quantization. That is, the coordinate $\mathbf{r}$ is specified by angles θ and φ with respect to $\mathbf{R}$ as axis. During the collision the internuclear line rotates through 180°, so that the quantization is with respect to a rotating coordinate system, but the differentiation $\partial/\partial Z$ is specified to be carried out with $\mathbf{r}$ fixed in space. This is illustrated in Fig. 8-6, where the rotation of AB about the center of mass C is shown. If the angle that $\mathbf{R}$ makes with the z axis is Θ, then

$$\sin \Theta = \frac{b}{R} \quad \text{and} \quad \cos \Theta = \frac{Z}{R} . \tag{8-68}$$

The plane of rotation is chosen to be the (x, z) plane and if (x', y', z') are the components of $\mathbf{r}$ with respect to the rotating axes with the z' axis along $\mathbf{R}$, and if (x, y, z) are the
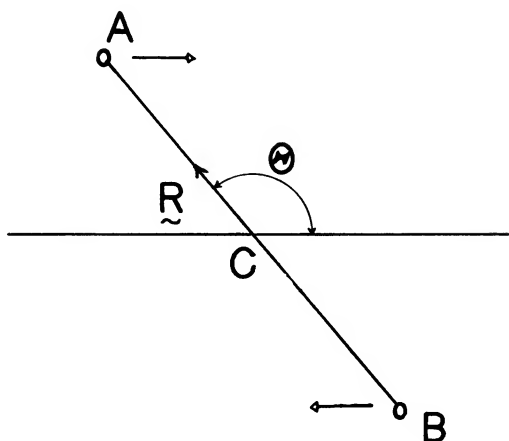
Figure 8-6.   Rotation of the internuclear line during charge exchange.

coordinates of **r** with respect to axes fixed in space, with z
in the direction of incidence, then

$$x' = x \cos \Theta + z \sin \Theta,$$
$$y' = y, \qquad\qquad\qquad\qquad (8\text{-}69)$$
$$z' = z \cos \Theta - x \sin \Theta.$$

The operation $\partial/\partial Z$ applied to the molecular function
$\chi_n(x',y',z',\mathbf{R})$ is:—

$$\frac{\partial}{\partial Z}\chi_n(x',y',z',\mathbf{R}) = \frac{\partial'}{\partial Z}\chi_n + \frac{d\Theta}{dZ}\left(z'\frac{\partial}{\partial x'} - x'\frac{\partial}{\partial z'}\right)\chi_n,$$

where $\partial'/\partial Z$ denotes the differentiation is to be taken with
x', y' and z' fixed. Since

$$\frac{d\Theta}{dZ} = -\frac{b}{R^2}, \qquad\qquad\qquad (8\text{-}70)$$

we have that

$$\boldsymbol{\gamma}_{nm} \cdot \hat{\mathbf{n}} = 2 \int d\mathbf{r} \left(\chi_n^* \frac{\partial'}{\partial Z} \chi_m \right) + \frac{i}{\hbar} \frac{2b}{R^2} \int d\mathbf{r} \left(\chi_n^* L_y' \chi_m \right),$$

$$(8-71)$$

where L_x, L_y, L_z are the components of the angular momentum operator (see Bates et al., 1953). The matrix elements of L_y' provide a strong coupling between wave functions χ_n or φ_n that differ in magnetic quantum number. These coupling terms represent the Coriolis force, arising from the rotation of the coordinate system in which the wave functions are defined, and cannot be neglected.

If atomic wave functions are used to define the χ_n and φ_m a choice is possible:— The axis of quantization may be fixed in space or alternatively taken to be the rotating nuclear line. Either choice is correct provided due care is taken that the differential operation $\partial/\partial Z$ is performed consistently, that is, in such a way that $\mathbf{r}$ is kept constant with respect to fixed axes and at the same time $\mathbf{b}$ is fixed.

Unitarity and time reversal

It is not difficult to show that the truncated set of equations using any linearly independent set of functions χ_n or φ_m satisfies the requirement of unitarity, expressed in this case by the requirement that the probability that some final state is attained is unity.[11]

$$\sum_n |A_n(b, \infty)|^2 + \sum_m |C_m(b, \infty)|^2 = 1,$$

where the sums run over the truncated sets. By placing the incident wave in each channel in turn, all the elements of the S matrix can be calculated, and time reversal invariance is also satisfied in that the S matrix is symmetrical.

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[11] Green (1966a).

8-3   EXPANSIONS BASED ON ATOMIC EIGENFUNCTIONS

In this section we shall discuss some of the applications of the impact parameter equations employing atomic wave functions centered on either A or B.

$$\chi_n(\mathbf{r}, \mathbf{R}) = \psi_{B_n}(\mathbf{r}_B) \exp(i\ell_1 \mathbf{k}_n \cdot \mathbf{r}_B)$$

$$\varphi_m(\mathbf{r}, \mathbf{R}) = \psi_{A_m}(\mathbf{r}_A) \exp(i\ell_2 \mathbf{K}_m \cdot \mathbf{r}_A).$$

(8-72)

In some applications, systems of more than one electron are considered, such as the proton-helium system

$$P + He \rightarrow P + He$$
$$\rightarrow H + He^+.$$

(8-73)

The general theory can be extended in obvious ways to the many electron system and the only new feature is that properly symmetrized wave functions should be used to take account of the identity of the electrons. This effect is quite small except at low velocities and can safely be neglected at incident energies in excess of 20-30 kev.

The two state approximation-excitation

It is interesting to examine the structure of the coupled equations in some simple cases. We shall start by writing the equations for excitation in a two state approximation, assuming that both the initial and final states of the target are described by spherically symmetrical wave functions $\psi_{B_0}(r_B)$ and $\psi_{B_1}(r_B)$. Equations (8-60), making the approximations (8-63) and (8-64) become

$$i\hbar v \frac{\partial A_0}{\partial Z} = V_{01}(Z) \left\{ \exp i \left[\frac{1}{\hbar v} \int_{-\infty}^{Z} (V_{00} - V_{11}) dZ - \left(\frac{\epsilon_1 - \epsilon_0}{\hbar v} \right) Z \right] \right\} A_1(Z),$$

(8-74a)

$$i\hbar v \, \frac{\partial A_1}{\partial Z} = V_{10}(Z)\left\{\exp i\left[-\frac{1}{\hbar v}\int_{-\infty}^{Z}(V_{00} - V_{11})\,dZ +\right.\right.$$

$$\left.\left. +\left(\frac{\epsilon_1 - \epsilon_0}{\hbar v}\right)Z\right]\right\}A_0(Z), \qquad\qquad (8-74b)$$

where

$$V_{10}(Z) = V_{01}(Z) = \int d\mathbf{r}_B \Psi_{B_1}^*(r_B)\,(V_{AB} + V_{Ae})\Psi_{B_0}(r_B),$$

$$\qquad\qquad\qquad\qquad\qquad (8-75)$$

and

$$V_{00}(Z) = \int d\mathbf{r}_B |\Psi_{B_0}(r_B)|^2\,(V_{AB} + V_{Ae}), \qquad (8-76a)$$

$$V_{11}(Z) = \int d\mathbf{r}_B |\Psi_{B_1}(r_B)|^2\,(V_{AB} + V_{Ae}). \qquad (8-76b)$$

In obtaining V_{nm} from the definitions (8-45), it has been assumed that Ψ_{B_n} satisfies the Schrödinger equation

$$\left(-\frac{\hbar^2}{2m}\nabla^2_{r_B} + V_{Be} - \epsilon_n^B\right)\Psi_{B_n} = 0, \qquad (8-77)$$

exactly, so that

$$\left(\bar{H} - \epsilon_n^B\right)\psi_{B_n} = (V_{AB} + V_{Ae})\psi_{B_n}. \qquad (8-78)$$

If the target has more than one electron, the target wave function will only be known in some approximation. It is then important not to assume that these functions satisfy a wave equation in evaluating the matrix elements V_{nm}, because such an assumption may lead to equations which do not obey time reversal invariance (obtained in our example by the condition $V_{01} = V_{10}$) and also the connection of the equations with the variational method will be removed.

The boundary conditions to be imposed on the integration of equation (8-74) are at $Z = -\infty$

$$A_0(b, Z = -\infty) = 1, \quad A_1(b, z = -\infty) = 0 \quad \text{all } b$$

and the cross section for a transition from $0 \rightarrow 1$ is

$$\sigma_{10} = 2\pi \int_0^\infty b \, |A_1(b, z = +\infty)|^2 \, db. \qquad (8\text{-}79)$$

The coupling terms in the equations (8-74) oscillate with a frequency that depends on the factor $(\Delta E/\hbar v)$, where ΔE is the energy difference between the states. Thus when ΔE is large the effective coupling will oscillate rapidly and the transition probability will be low. When ΔE is small the two states concerned will be strongly coupled. The two state approxima- tion is particularly useful when ΔE for the pair of states concerned is smaller than the corresponding energy differences between either of the states and any other state. As $v \to 0$, the transition probability is also expected to decrease rapidly except in the case of resonance for which $\Delta E = 0$. The terms involving V_{00} and V_{11} in the exponents represent the first order perturbation of the energy of the system by the interaction. The lowest order approximation to $A_1(b, \infty)$ is obtained by set- ting $A_0(z) = 1$ on the right hand side of (8-74b) and ignoring V_{00} and V_{11}. On integrating we have

$$|A_1(b, \infty)|^2 \simeq \frac{1}{\hbar^2 v^2} \left| \int_0^\infty dZ V_{10}(Z) \exp\left[\frac{i}{\hbar v}(\epsilon_1 - \epsilon_0)Z\right] \right|^2.$$
$$(8\text{-}80)$$

The approximations leading to (8-80) are the same as those of the Born approximation and it can be shown that the cross sec- tion obtained is in fact identical with that obtained in the Born approximation (Arthurs, 1961). Setting $A_0 = 1$, but retaining V_{00} and V_{11} leads to the semi-classical version of the distor- ted wave Born approximation

$$|A_1(b,)|^2 \simeq \frac{1}{\hbar^2 v^2} \left| \int_0^\infty dZ V_{10}(Z) \exp i \left[\frac{1}{\hbar v}(\epsilon_1 - \epsilon_0)Z - \right. \right.$$

$$\left. \left. - \int_{-\infty}^Z (V_{00} - V_{11}) \, dZ \right] \right|^2. \qquad (8\text{-}81)$$

Unless $V_{00} \approx V_{11}$, the effect of distortion may be consider- able, reducing the cross section from that given by the Born approximation. Neither of these approximations guarantees the unitarity of the theory and the failure of these approximations

is often signalled when $|A_1(b,\infty)|^2$ exceeds unity for some range of impact parameter b.

For proton excitation of helium to 2^1P and 3^1P levels, the distorted wave calculations of Bell (1961) can be compared with the measurements of Thomas and Bent, to which we have already referred. Fig. 8-7 shows the calculated and measured cross sections for excitation of the 3^1P level and in this case it is seen that the agreement is very good down to 100 kev, well below the energies at which the Born approximation is valid (500 kev). Other calculations in the distortion approximation are discussed by Bates (1962) and deHeer (1966); in
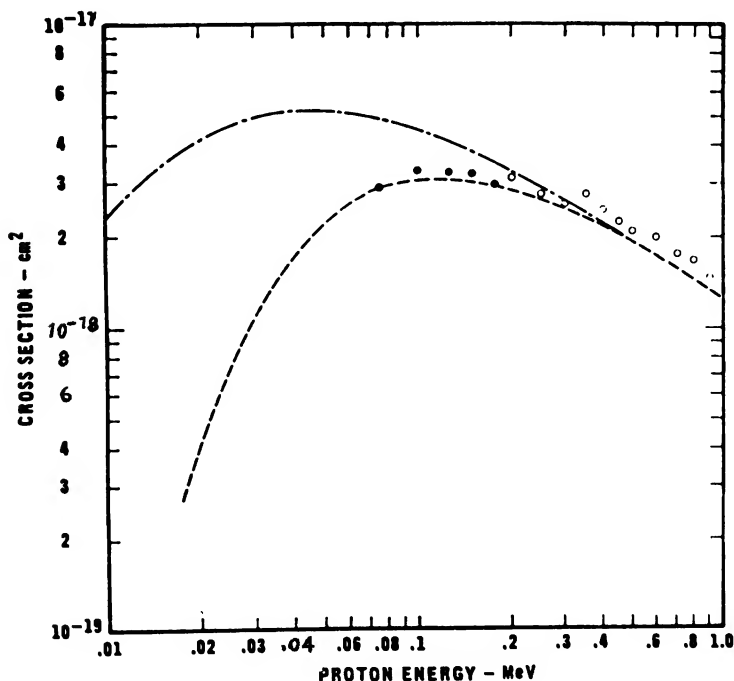
Figure 8-7.   Proton excitation of helium to the 3^1P level.

      o   Proton impact experimental.

      ●   Deuteron impact experimental (Thomas and Bent, 1967).

  -.-.-   Born approximation (Bell, 1961).

  -----   Distorted wave approximation (Bell, 1961).

general the effect of distortion increases with increasing charge of the nuclei, that is, it is greater for

$$a + H(1s) \rightarrow a + H(2s)$$

than for

$$P + H(1s) \rightarrow P + H(2s)$$
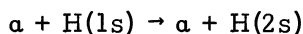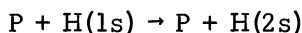
and greater for transitions which receive contributions mainly from small impact parameters (close collisions), than for those that receive contributions from distant collisions.

The two state approximation–charge exchange

In the case of charge exchange some new features appear in the coupled equations. Consider the two state approximation in which the initial wave function of the electron bound to the nucleus B is ψ_{B_0} and the final wave function bound to the nucleus A is ψ_{A_1} and again we shall suppose that ψ_{B_0} and ψ_{A_1} are spherically symmetrical. The impact parameter equations are

$$i\hbar v \frac{\partial A_0}{\partial Z} = -i\hbar v S_{01} \frac{\partial C_1}{\partial Z} e^{i\mu} + [H_{01} - U_{11} S_{01}] e^{i\mu} C_1,$$
(8-82a)

$$i\hbar v \frac{\partial C_1}{\partial Z} = -i\hbar v S_{01}^* \frac{\partial A_0}{\partial Z} e^{-i\mu} + \left[T_{10} - V_{00} S_{01}^*\right] e^{-i\mu} A_0,$$
(8-82b)

where

$$S_{01} = \int d\mathbf{r} \psi_{B_0}^* (r_B) \psi_{A_1} (r_A) \exp\left(i \frac{m\mathbf{v} \cdot \mathbf{r}}{\hbar}\right),$$
(8-83a)

$$H_{01} = \int d\mathbf{r} \psi_{B_0}^* (r_B) \psi_{A_1} (r_A) \exp\left(i \frac{m\mathbf{v} \cdot \mathbf{r}}{\hbar}\right) (V_{AB} + V_{Be}),$$
(8-83b)

$$T_{10} = \int d\mathbf{r} \psi_{A_1}^* (r_A) \psi_{B_0} (r_B) \exp\left(-i \frac{m\mathbf{v} \cdot \mathbf{r}}{\hbar}\right) (V_{AB} + V_{Ae}),$$
(8-83c)

$$\mu = \frac{1}{\hbar v} \left\{ \int_{-\infty}^{Z} (V_{00} - U_{11}) \, dZ - \left(\epsilon_1^A - \epsilon_0^B \right) Z \right\}, \quad (8\text{-}83d)$$

and

$$U_{11} = \int d\mathbf{r}_A |\psi_{A_1}(\mathbf{r}_A)|^2 (V_{AB} + V_{Be}),$$

where V_{00} is given by (8-76a) and again use has been made of the wave equation satisfied by ψ_{B_0} and ψ_{A_1}. The matrix elements connecting the two channels S_{01}, H_{01} and T_{01} contain as a factor $\exp(\pm im \mathbf{v} \cdot \mathbf{r}/\hbar)$, which arise from the exponential factors in (8-72). This factor represents the change in momentum of the electron due to its translation motion, when it is transferred from nucleus B to nucleus A, which are moving with relative velocity $\mathbf{v}$. As v increases, the oscillation of this factor is responsible for a rapid decrease in the matrix elements, compared with those referring to direct excitation or scattering (V_{00}, U_{00}, U_{01} etc.) in which the exponential factor does not appear

Solving the equations (8-82a) and (8-82b) for $\partial A_0/\partial Z$ and $\partial C_1/\partial Z$, we find

$$i\hbar v(1 - |S_{01}|^2) \frac{\partial A_0}{\partial Z} = -S_{01}[T_{10} - V_{00}S_{01}^*]A_0 +$$

$$+ [H_{01} - U_{11}S_{01}] \exp(i\mu)C_1,$$

$$i\hbar v(1 - |S_{01}|^2) \frac{\partial C_1}{\partial Z} = -S_{01}^*[H_{01} - U_{11}S_{01}]C_1 +$$

$$+ [T_{10} - V_{00}S_{01}^*] \exp(-i\mu)A_0.$$

The diagonal terms can be eliminated by redefining A_0 and C_1 but we shall not stop to do this here. The effect is to slightly modify the distortion factor μ. The important point to notice is the appearance of effective interactions of the form $[T_{10} - V_{00}S_{01}^*]$, which correspond exactly to the interactions appearing in the first order exchange approximation. The matrix elements of V_{AB} exactly cancel between the two terms and between the similar pairs of terms occurring in the equations. The theory does not therefore depend on the value of V_{AB}, and this is consistent with the assumption of the straight trajectories for the heavy particles. The Born approximation to these

equations is given by

$$C_1(b, \infty) = \frac{1}{i\hbar v} \int_{-\infty}^{\infty} dZ \left[\frac{T_{10} - V_{00}S_{01}^*}{1 - |S_{01}|^2} \right] \exp -\frac{i}{\hbar v}\left(\epsilon_0^B - \epsilon_1^A\right)Z,$$

(8-84)

and the distorted wave approximation can be written down in a similar way.

Symmetrical resonance

When the nuclei A and B are identical, we may proceed, as in the theory of the scattering of electrons by hydrogen atoms, to define amplitudes with a definite symmetry, and the coupled equations will correspondingly separate into two sets. In place of (8-35), the symmetrized expansion is

$$\Psi(\mathbf{r}, \mathbf{R}) = \sum_n \left[F_n^{\pm}(\mathbf{R})\chi_n(\mathbf{r}, \mathbf{R}) \pm F_n^{\pm}(-\mathbf{R})\varphi_n(\mathbf{r}, \mathbf{R}) \right], \quad (8-85)$$

where in the definitions of χ_n and φ_n, we now have that $\psi_{A_n}(\mathbf{x}) = \psi_{B_n}(\mathbf{x})$. The functions $F_n^{\pm}(\mathbf{R})$ satisfy the asymptotic conditions

$$F_n^{\pm}(\mathbf{R}) \sim \delta_{no} \exp(i\mathbf{k_0} \cdot \mathbf{R}) + f_{no}^{\pm}(\theta_R) \frac{e^{ik_nR}}{R}, \quad (8-86)$$

and in terms of the scattering amplitudes f_{no}, g_{no} we have

$$f_{no}^{\pm}(\theta_R) = f_{no}(\theta_R) \pm g_{no}(\pi - \theta_R). \quad (8-87)$$

The cross sections for unpolarized beams depend on whether A and B are fermions or bosons. For example, if A and B are protons, then for an unpolarized beam the total cross section for elastic scattering is

$$\sigma(e\ell) = \int d\Omega\,(\hat{R}) \left[\frac{3}{4} |f_{no}^-(\theta_R)|^2 + \frac{1}{4}\left|\left(f_{no}^+(\theta_R)\right)\right|^2 \right]$$

$$= \int d\Omega\,(\hat{R}) \left[|f_{no}(\theta_R)|^2 + |g_{no}(\pi - \theta_R)|^2 - \right.$$

$$\left. - \text{Re}\left[f_{no}^*(\theta_R) g_{no}(\pi - \theta_R) \right] \right]. \quad (8-88)$$

If A and B are alpha particles with spin zero we must take f_{oo}^+ only and

$$\sigma(el) = \int d\Omega \, (\hat{R}) \, | f_{oo}^+ (\theta_R) |^2$$

$$= \int d\Omega \, (\hat{R}) \left[| f_{oo} (\theta_R) |^2 + | g_{oo} (\pi - \theta_R) |^2 + \right.$$

$$\left. + 2 \text{Re} \left[f_{oo}^* (\theta_R) g_{oo} (\pi - \theta_R) \right] \right]. \qquad (8-89)$$

Except at low energies, $f_{oo}(\theta)$ is large only for $\theta \approx 0$ and $g_{oo}(\theta)$ is large only for $\theta \approx \pi$, so as we have noted before separate elastic and exchange cross sections can be defined in terms of $|f_{oo}|^2$ and $|g_{oo}|^2$ respectively. Of course under these circumstances there are no interference effects due to nuclear identity, but for the p-H collision these effects do not become important until the incident energy is less than 3 ev (Smith, 1967). It sometimes happens that A and B possess the same charge, but are different in mass. The wave function is then symmetrical or anti-symmetrical under reflections about the center of charge of the system, which leads to some simplication of the equation. In this case the exchange and elastic cross sections are always well defined.

To illustrate the uncoupling of the equations in the case of resonance consider the two state equations (8-82). We find that

$$S_{o1} = S_{o1}^*, \quad H_{o1} = T_{1o}, \quad V_{oo} = U_{11}, \quad \mu = 0,$$

so the equations become

$$\hbar v i \, \frac{\partial A_o}{\partial Z} = h_{oo} A_o + h_{o1} C_1, \qquad (8-90a)$$

$$\hbar v i \, \frac{\partial C_1}{\partial Z} = h_{oo} C_1 + h_{o1} A_o, \qquad (8-90b)$$

with

$$h_{oo} = \frac{-S_{o1} [T_{1o} - V_{oo} S_{o1}]}{(1 - S_{o1}^2)} \qquad (8-91a)$$

$$h_{o1} = \frac{T_{1o} - V_{oo} S_{o1}}{(1 - S_{o1}^2)}, \qquad (8-91b)$$

the equations uncouple if we define $A^{\pm} = A_0 \pm C_1$, giving

$$\hbar v i \frac{\partial A^{\pm}}{\partial Z} = (h_{00} \pm h_{01})A^{\pm}.$$

Integrating this equation and combining A^+ and A^- to form C_1 we get

$$C_1 = -i \exp\left\{-\frac{i}{\hbar v}\int_{-\infty}^{Z} h_{00} dZ\right\} \sin\left[\frac{1}{\hbar v}\int_{-\infty}^{Z} h_{01}\ dZ\right]. \quad (8\text{-}92)$$

As S_{01} and V_{00} and $\mathrm{Re}T_{10}$ are real and symmetrical in Z and $\mathrm{Im}T_{10}$ is anti-symmetrical in Z, we have that

$$|C_1(b, \infty)|^2 = \sin^2\left[\frac{1}{\hbar v}\int_{-\infty}^{\infty} \mathrm{Re}(h_{01}) dZ\right]. \quad (8\text{-}93)$$

In the case of symmetrical resonance, equation (8-93) predicts that the probability of charge transfer will oscillate as a function of impact parameter for fixed energy E, and for a fixed value of impact parameter will oscillate as a function of energy. Because semi-classical conditions hold, the angle of scattering will be determined by the impact parameter, through equations (2-137) and (2-139), $(b = L/v)$, so that at a fixed angle of scattering the probability of charge transfer is expected to oscillate as a function of energy. The angular distribution can be worked out using a transformation like (2-102), but from the discussion leading to equation (2-149) the scattering amplitude is seen to be equal to $(d\sigma_c/d\Omega)^{1/2} \exp(i\beta)$, where $d\sigma_c/d\Omega$ is the classical differential cross section and β is the semi-classical phase. The amplitudes $f_{no}(\theta)$, $g_{no}(\theta)$, (see 8-88) are

$$f_{no}(\theta) = \left|\frac{d\sigma_c}{d\Omega}\right|^{\frac{1}{2}} A_0(\theta) \exp\left[\frac{i}{\hbar v}\int_{-\infty}^{\infty} V_{00}\ dZ + \frac{\pi}{4}i\right] \quad (8\text{-}94a)$$

$$g_{no}(\theta) = \left|\frac{d\sigma_c}{d\Omega}\right|^{\frac{1}{2}} C_1(\theta) \exp\left[\frac{i}{\hbar v}\int_{-\infty}^{\infty} U_{nn}\ dZ + \frac{\pi}{4}i\right] \quad (8\text{-}94b)$$

where $(d\sigma_c/d\Omega)^{\frac{1}{2}}$ is the classical cross section for scattering in the potential field V_{00} or U_{nn}. The experiments measure

the ratio of the charge exchange cross section to the total (elastic and charge exchange) cross section, $P_{CE}(\theta)$, giving

$$P_{CE}(\theta) = \frac{|C_1(\theta)|^2}{|A_0(\theta)|^2 + |C_1(\theta)|^2}. \tag{8-95}$$

In the present two state approximation, $|C_1|^2$ is given by (8-93) and

$$|A_0(\theta)|^2 = \cos^2\left[\frac{1}{\hbar v}\int_{-\infty}^{\infty} Re(h_{01})dZ\right] \tag{8-96}$$

so that $P_{CE}(\theta)$ oscillates between 0 and 1.

Damping of these oscillations can occur in two distinct ways. It may be necessary to include further terms in the expansion of the wave function and if the probability of excitation or capture into an excited state is appreciable, the probability of capture into the ground state will be less than unity and $P_{CE}(\theta)$ will oscillate with an amplitude less than unity. Damping can also occur, when there are two distinct classical paths that the system can follow. For example we shall see that in an approximation based on molecular wave functions, the situation is different, and the phase of the amplitude is different on each of the classical trajectories associated with U_{nn} and V_{00} and interference effects produce damping of the oscillations in $P_{CE}(\theta)$.

Applications

Numerical calculations based on the two state approximation have been carried out for the reaction p + H(1s) → H(1s) + p by McCarroll (1961) in the energy range 10 kev to 1 mev. Above 25 kev the coupling is weak and the distorted wave version of the theory is adequate but below 25 kev the coupling is strong. However the work of Lovell and McElroy (1965) shows that the two state approximation is inadequate and that it is necessary to include at least the states with n = 2. At the higher energies, the calculated cross section lies close to, but above, the Born approximation. The total cross section for electron capture including capture into all excited states has been measured up to 250 kev (Fite et al., 1962; McClure, 1966; Whitthower et al., 1966).

To compare the results of McCarroll

with these experiments, the cross sections for capture into
excited states must be computed. This has been done for
capture into the 2s and 2p states by McElroy (1963), who em-
ployed the distorted wave solutions to equations (8-8 a,b).
The distortion terms containing S_{01}^* in (8-8 b) may be ignored
to a good approximation, giving

$$C_1 (\infty) \approx \frac{1}{i\hbar v} \int_{-\infty}^{\infty} [T_{10} - V_{00}S_{01}^*] \exp(-i\mu (Z)) \, dZ. \qquad (8-97)$$

From the cross section in the Brinkman-Kramers app-
roximation, the capture cross section into excited S states of
level n is found to be roughly proportional to $(1/n^3)$. A
correction to the computed cross section for capture into states
with $n > 2$ can be made on this basis, and is found to be quite
small.

The total cross section in the two state approximation
is shown in Fig. 8-4 and is seen to agree with the experimental
results between 25-50 kev, but by 120 kev the calculated
cross section is too large by some 60%. The Born approxima-
tion provides cross sections at the higher energies which are
rather small, while the impulse approximation gives cross
sections which are much smaller and in complete disagreement
with the measurements.

At the lower energies, the most complete investigation
has included the 2s and 2p of hydrogen in both the direct and
rearranged terms, χ_m and φ_m (Wilets and Gallaher, 1966).
This approximation allows the cross section to be calculated
from capture into the (1s), (1s) and (2p) states and at the same
time the (2s) and (2p) excitation cross sections are given.
Some calculations in which the states with $n = 3$ were included
indicated that it was sufficient to consider states with $n \leq 2$.
The total cross section for capture into the 2s state is compar-
able with that obtained in the distorted wave approximation by
McElroy, but the capture cross section into the (2p) state is
much lower than the distorted wave result, illustrating the
effects of coupling in this case. The 2p excitation and cap-
ture cross sections are about half those measured in the energy
range up to 100 kev by Stebbings et al. (1965) but the experi-
mental cross sections are themselves uncertain to about 50%.
These results are illustrated in Figs. 8-8 and 8-9.

The variation of the cross section for capture with
energy from 1 to 60 kev at fixed scattering angle has been
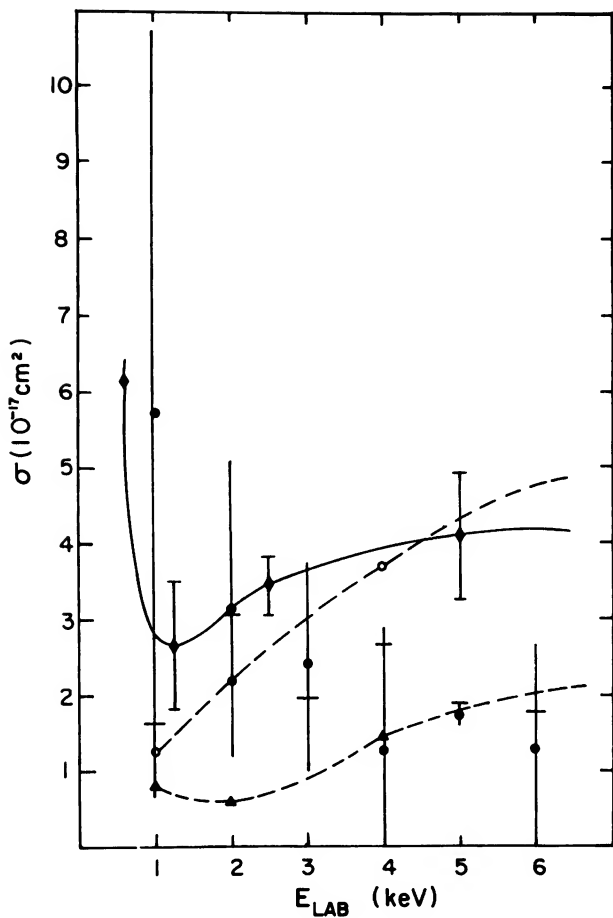
Figure 8-8.   The cross section for the charge transfer reaction p + H(1s)→H (2p) + p.
   ◆   Experimental data of Stebbings et al. (1965).
   ●   Experimental data of Gailly (1968), Gailly et al. (1968).
   Upper dashed curve: Cross section calculated in a four-state Sturmian ex-
                    pansion (Gallaher and Wilets, 1968).
   Lower dashed curve: Cross section calculated in a four-state hydrogenic
                    expansion (Gallaher and Wilets, 1966).
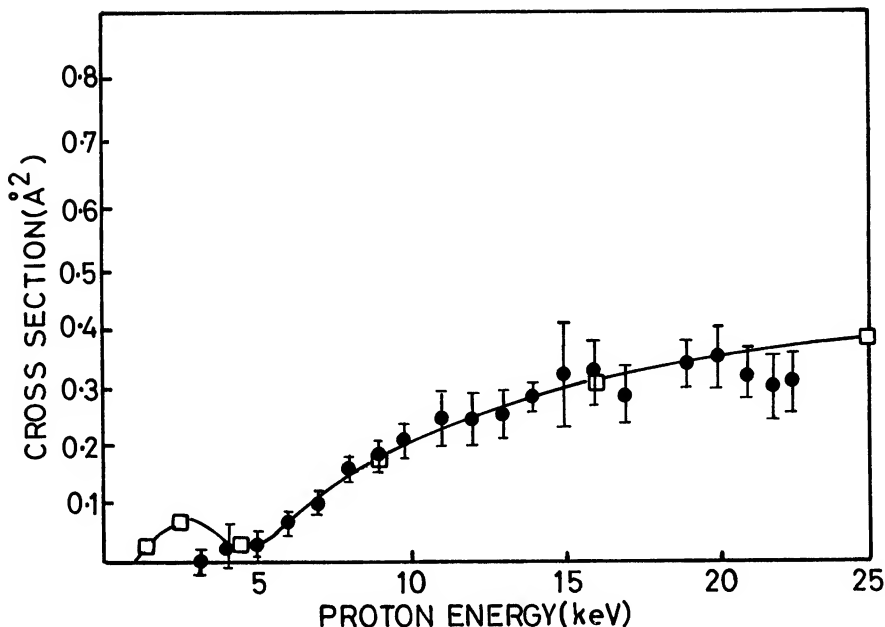
Figure 8-9.   The cross section for the charge exchange reaction

$$p + H(1s) \rightarrow H(2s) + p.$$
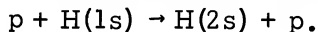
Experimental data are due to Bayfield (1968).

measured by Everhart (1963), Lockwood and Everhart (1962) and Everhart et al. (1963). The angle of scattering in the laboratory of the incident proton is 3°. The bulk of the cross section arises from much smaller angles, so scattering at 3° can be properly termed large angle scattering and corresponds to very close collisions with small impact parameters. The results, Shown in Fig. 8-10, show the damped oscillations that were discussed above. The two state approximation which predicts no damping is clearly inadequate, but the results of Wilets and Gallaher are in reasonable agreement with the measurements, although the turning points do not occur at the same
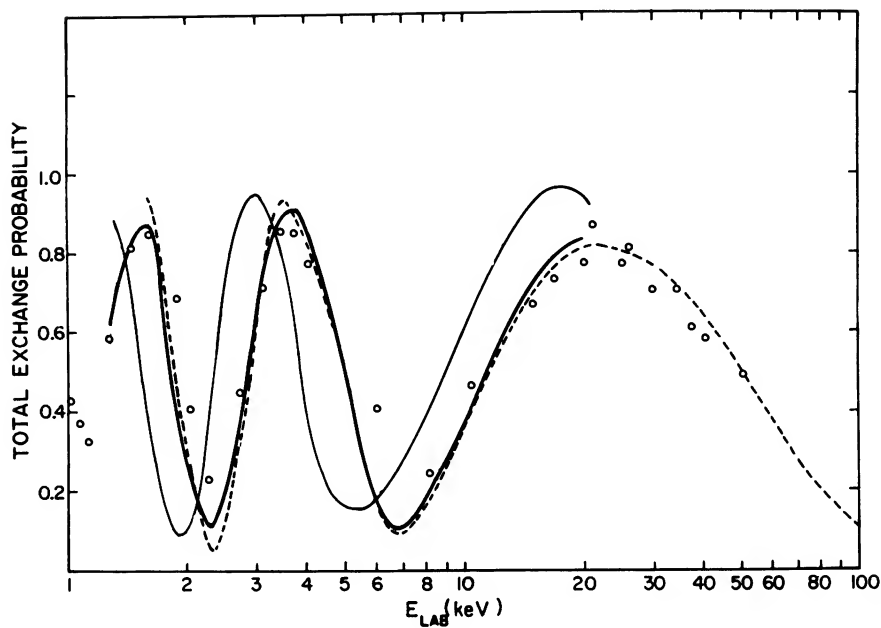
Figure 8-10. Differential cross section at fixed angle (3°) for the reaction

$$p + H(1s) \rightarrow H(1s) + p.$$
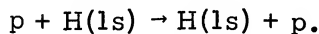
o   Experimental data (Everhart and Helbig, 1965).
Calculated cross section.

              ━━━   4-state Sturmian expansion.
              - - - -   3-state Sturmian expansion.
              _____   4-state hydrogenic expansion.

energies as the measured ones. Better agreement is obtained with the expansions based on molecular wave functions and on Sturmian functions (Wilets and Gallaher, 1967); that will be described later.

Another reaction that has been studied in some detail using the expansion based on atomic wave functions is the reaction

$$H^+ + He(1s^2) \rightarrow H(n\ell) + He^+(1s).$$
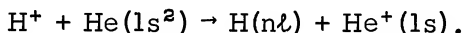
Green et al. (1965) solved the two state approximation in which the ground state wave function of hydrogen was included in the final state, while Sin Fai Lam (1967) extended this work by including the (2s) and (2p) state of hydrogen in the final wave function. In the initial state the helium ground state wave function was of a simple variational type, but the results are not very sensitive to the precise form of this function (Bransden and Sin Fai Lam, 1966). In this example the calculated probability of capture in the ground state of hydrogen is not altered very much by adding the (2s) and (2p) hydrogen states, but the coupling between the (2s) and (2p) states is large and must be included if the capture cross sections into these states is to be calculated.

The total capture cross section, calculated from the ground state capture cross section by making an allowance for capture into all excited states by the Born approximation, agrees with the experimental cross section over the energy range 15 kev - 100 kev (the experimental cross section is shown in Fig. 8-5). Above 100 kev, the calculated cross section is clearly too large. For example at 400 kev the calculated cross section is $3.5 \times 10^{-19} cm^2$ and the experimental cross section is $2 \times 10^{-19} cm^2$. This may be a reflection of the importance of the continuum intermediate states in the expansion as suggested by the impulse and second Born approximations. Below 10 kev, the approximation fails badly, the theoretical predictions being too small by a factor of 14 at 1 kev. At these low energies it is likely that an expansion based on molecular wave functions would be more successful.

The calculated cross sections for capture into the (2s) and (2p) states are shown in Figs. (8-11) and (8-12), together with the Born approximation calculations of Mapleton (1961) and experimental measurements. Although the experimental results disagree
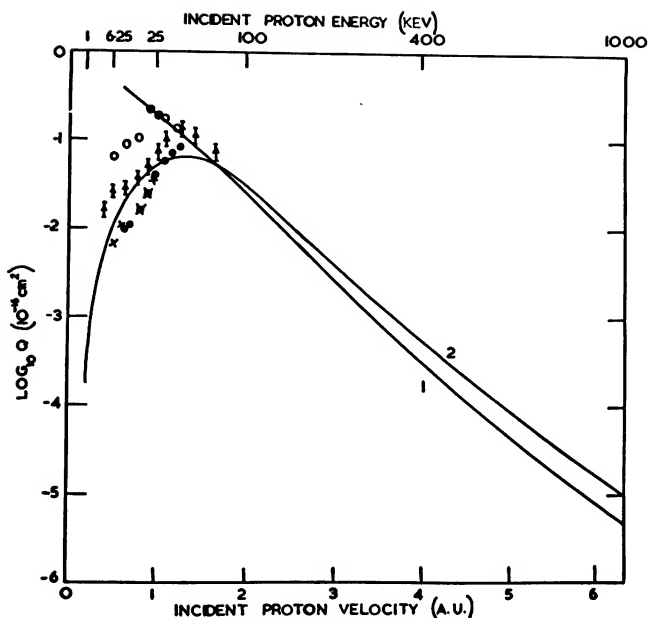
Figure 8-11.   Cross section for the charge exchange reaction

$$p + He(1s^2) \rightarrow H(2s) + He^+(1s).$$
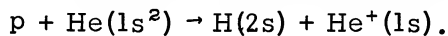
Experimental results:

- **O**   Colli et al. (1962).
- **●**   Andreev et al. (1966).
- **X**   Jaecks et al. (1965).
- **↨**   Dose (1966).

Calculated results:

1.   Born approximation (Mapleton, 1961).
2.   Atomic expansion (Sin Fai Lam, 1967).
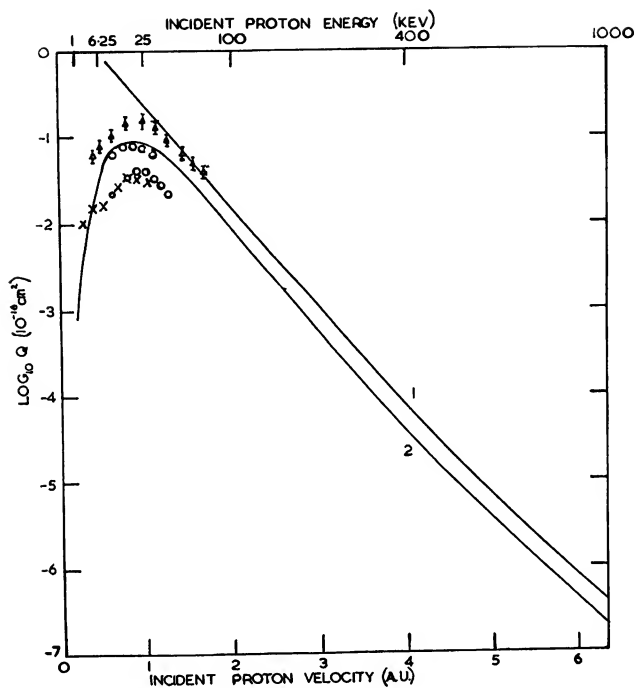
Figure 8-12.   Cross section for the charge exchange reaction

$$p + He(1s^2) \rightarrow H(2p) + He^+(1s).$$

Experimental results:
         ✕   Pretzer et al. (1963).
         O   de Heer et al. (1963)
         Ⱶ   Dose (1966).
Calculated results:
         1.   Born approximation (Mapleton, 1961).
         2.   Atomic expansion (Sin Fai Lam, 1967).

between themselves considerably, it can be stated that the calculated cross section is of the right order of magnitude and has the correct shape as a function of energy.

It is probably safe to conclude that the cross sections for non-resonance charge transfer are given reliably by an expansion based on atomic wave functions at energies near the cross sections' maximum, in this case near 25 kev. Electron capture from hydrogen by alpha particles and from helium by helium ions are among the other processes that have been investigated in this approximation (McElroy, 1963; McCarroll and McElroy, 1962; Basu et al., 1966; Fulton and Mittleman, 1966; Sural et al., 1967; see also Bransden, 1965), but in the most extensive calculation (Sural et al., 1967) the momentum transfer of the captured electron was neglected so that the results are likely to be in error on this account.

8-4   SPECIAL EXPANSIONS AND METHODS

The methods of expansion into atomic or molecular eigenfunctions is in principle applicable to all collisions, but for the three body problem some special methods have been developed that are very promising.

Expansion in Sturmian functions

In so far as the impact parameter approximation is valid, the scattering problem reduces to solving the time dependent Schrödinger equation (8-65), with the specified boundary conditions. The wave function $\Psi(\mathbf{r},t)$ can be expanded in any complete set of functions of $\mathbf{r}$, and we are not limited to its usual atomic or molecular functions that have the disadvantage of possessing a continuum, which is difficult to deal with. A complete basis is provided by the Sturmian functions which form a discrete set and an expansion based on these functions has been used by Gallaher and Wilets (1968). The basis functions are

$$f_{\ell,m,n}(\mathbf{r}) = r^{-1} S_{n,\ell}(r) Y_{\ell,m}(\theta,\varphi), \qquad (8\text{-}99)$$

where $S_{\ell,n}(r)$ satisfies (atomic units)

$$\left(-\frac{1}{2}\frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{2r^2} - \frac{a_{n_\ell}}{r} \right) S_{n,\ell}(r) = E_\ell S_{n,\ell}(r), \quad (8\text{-}100)$$

and

$$E_\ell = -\frac{1}{2(\ell + 1)^2} \,.$$

If the boundary condition is imposed that $S_{n,\ell}(r)$ vanishes as $r \to \infty$, then for a given fixed value of E_ℓ, a_{n_ℓ} is determined as an eigenvalue of equation (8-100). The functions $S_{n,\ell}(r)$ are discrete hydrogenic functions, apart from a factor, and E_ℓ can be chosen so that the first Sturmian function for each ℓ coincides with the corresponding hydrogenic function. The wave function $\Psi(\mathbf{r},t)$ is expanded in terms of Sturmian functions centered about each nucleon A and B, just as in the hydrogenic expansion. The expansion coefficients are obtained by solving similar coupled equations, and the physical amplitudes are found by expanding the Sturmian function in terms of hydrogenic functions. Each Sturmian function includes a contribution from the continuum of hydrogenic functions, so that the effect of the continuum is included to some extent. The convergence of the expansion has been tested by including up to ten states and appears to be satisfactory. The calculations based on the 1s, 2s and 2p states, centered about both nuclei, are compared with the results of the hydrogenic expansion and with experiment in Figs. 8-8 and 8-9. Close agreement is shown with the 2p capture and excitation cross section. However, as remarked earlier, the experimental cross sections are subject to some uncertainty. Almost perfect agreement is shown between the experimental cross section at fixed angle and the Sturmian calculations, and in this respect the results are certainly superior to those of the hydrogenic expansion.

Expansion in spherical harmonics

It is always possible to expand the wave function in a series of spherical harmonics which have as their argument the polar angles of $\mathbf{r}$,

$$\Psi(\mathbf{r},t) = \sum_{\ell,m} f_{\ell,m}(r,t) Y_{\ell,m}(\theta,\varphi). \tag{8-101}$$

Coupled equations for the radial functions $f_{\ell,m}$ are then found that are similar to those derived by Temkin for electron scattering by hydrogen (see Chapter 5). In this form, it is not easy to see how to apply the boundary conditions of the problem, so

Cheshire and Sullivan have considered Ψ as a function of $\mathbf{r}_B$, the coordinate joining the electron to the nucleus B, rather than of $\mathbf{r}$ the center of mass coordinate. They then expand

$$\Psi(\mathbf{r}_B, t) = \sum_{\ell, m} \varphi_{\ell, m}(\mathbf{r}_B, t) Y_{\ell, m}(\theta_B, \varphi_B) \qquad (8\text{-}102)$$

and solve the coupled equation for $\varphi_{o,o}$ and $\varphi_{\ell, m}$ ignoring higher order terms. The boundary conditions are that as $t \to -\infty$ the wave function must represent a proton incident in a hydrogen atom in the ground state,

$$\varphi_{\ell, m}(\mathbf{r}, t) \underset{t \to -\infty}{\approx} \varphi_o(\mathbf{r}) \, e^{-i\epsilon_o t} \, \delta_{\ell, 0} \, \delta_{m, 0}. \qquad (8\text{-}103)$$

This procedure is equivalent to including all s and p states of hydrogen in the expansion terms based on the target (χ_m), but does not explicitly include any of the rearranged terms, represented by the expansion based on the projectile (φ_m). Because of this only excitation cross sections were computed. The (2p) excitation cross section exceeded that computed by Wilets and Gallaher, using the two centered hydrogenic expansion, by about a factor of three at 25 kev and this illustrates that the terms in the wave function that allow for charge exchange are most effective in lowering excitation cross sections at these energies. (Other interesting discussions of the effects of the continuum in the hydrogenic expansions may be consulted in Cheshire (1964, 1965) and McDowell et al. (1968).)

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Chapter 9

SLOW COLLISIONS BETWEEN ATOMS

9-1   EXPANSION IN MOLECULAR WAVE FUNCTIONS AND LOW ENERGY SCATTERING

In the semi-classical approximation, slow collisions between atoms and ions can be discussed in terms of the coupled equations (8-60). If the kinetic energy of the heavy particles were zero, then the full Hamiltonian H would coincide with the electronic Hamiltonian $\bar{H}$ defined in (8-43). The eigenfunctions of $\bar{H}$ are the usual electronic molecular wave functions that are calculated as functions of $\mathbf{r}$ for a fixed intermolecular distance R. This suggests that a good approximation at low energies is to take the functions χ_n and φ_m, introduced in Chapter 8, to be these molecular wave functions, or combinations of such wave functions. The omitted nuclear kinetic energy $(-\hbar^2/2\mu\nabla_R^2)$ is then the operator perturbing the system and the cross sections for excitation or charge exchange are determined by the matrix elements of this operator. When this perturbation is small, the transition is said to take place adiabatically.

The two centers problem

As in the last chapter, we shall examine the problem of one active electron moving in the field of two heavy particles A and B. The molecular wave functions $\Psi_n(\mathbf{r},\mathbf{R})$ are then defined to be the bounded solutions of the equations

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$$[\bar{\bar{H}} - \epsilon_n(R)]\psi_n(\mathbf{r},\mathbf{R}) = 0,$$

or

$$\left[-\frac{\hbar^2}{2m}\nabla_r^2 + V_{Ae} + V_{Be} + V_{AB} - \epsilon_n(R)\right]\psi_n(\mathbf{r},\mathbf{R}) = 0. \quad (9-1)$$

where $\mathbf{R}$ enters as a fixed parameter. The internuclear potential is a constant, for fixed R, so that the total energy $\epsilon_n(R)$ is just the sum of V_{AB} and an electronic energy $\epsilon_n'(R)$,

$$\epsilon_n(R) = V_{AB} + \epsilon_n'(R). \quad (9-2)$$

The system is symmetrical with respect to rotations about the internuclear axis, so that the component of the angular momentum along the internuclear axis, λ, is a good quantum number. The eigenvalues of the Hamiltonian will depend on $|\lambda|$ rather than λ because the Hamiltonian is invariant under the reflections $(\mathbf{r} \to -\mathbf{r}; \ \mathbf{R} \to -\mathbf{R})$. Two further quantum numbers are required to specify a state completely. One way of choosing these numbers is to consider the united atom limit, in which the nuclei A and B coincide, $(R \to 0)$, forming a nucleus of charge $(Z_A + Z_B)$. In that case, the wave function is hydrogenic and is specified by the principal quantum number n, the orbital angular momentum ℓ and a magnetic number m. In this limit λ coincides with m, so that λ ranges in integer steps between $-\ell$ and $+\ell$. The states then can be designated as $1s\sigma$, $2p\sigma$, $2p\pi$, and so on, where $\sigma, \pi, \delta \ldots$ stand for $|\lambda| = 0,1,2,\ldots$. If there is more than one electron the component of the angular momentum along the axis is still a constant of the motion. In this case the total component of the angular momentum is designated by $\Sigma, \Pi, \Delta, \ldots$ for $|\sum_i \lambda_i| = 0,1,2,\ldots$. The quantum numbers n and ℓ do not represent constants of the motion at any finite separation of the nuclei.

In the limit of very large R, the electron must become attached either to one nucleus or the other. A correlation diagram can then be constructed which relates the states defined in the united atom limit to those in the separated limit. A diagram for the system H_2^+ is shown in Fig. 9-1. In constructing such a diagram, the "no-crossing rule" may be used which states that two levels with the same symmetry properties cannot cross as we let R vary from $R = 0$ to $R = \infty$. The proof, due to Neumann and Wigner (1929) and
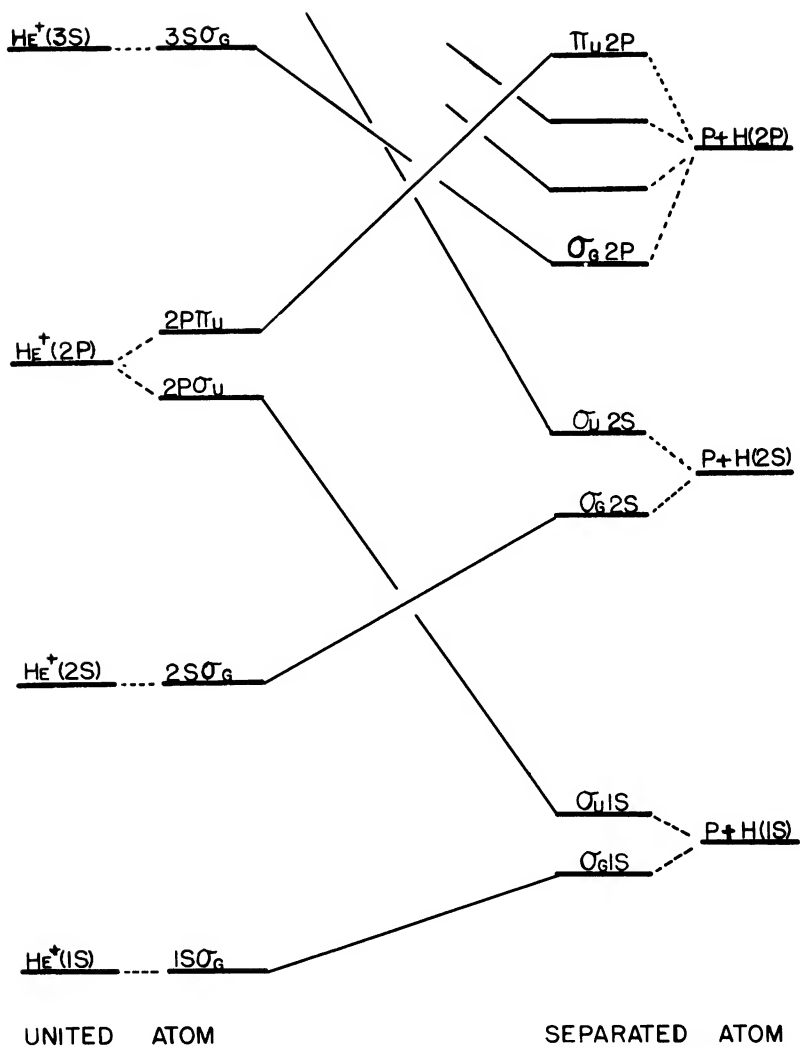
Figure 9-1.   Correlation diagram for the hydrogen molecular ion.

Teller (1936) is very simple. Suppose all the molecular wave functions are known except for two, φ_1 and φ_2, which may be taken as orthogonal to one another and to all the other functions. Then the energy levels are given by the roots of the equation

$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{vmatrix} = 0, \qquad (9-3)$$

where $H_{ij} = (\varphi_i, H\varphi_j)$. For the levels to cross the roots must be equal, that is $(H_{11} - H_{22})^2 + 4H_{12}^2 = 0$. When φ_1 and φ_2 belong to different symmetries, $H_{12} = 0$ and it is quite possible that the crossing will occur if, for a certain value of R, $H_{11} = H_{22}$. If φ_1 and φ_2 have the same symmetry then H_{12} will in general be non-zero and the levels cannot cross. Accidental crossing cannot be ruled out in which, by coincidence, $H_{12} = 0$ at the same value of R as $H_{11} = H_{22}$. This rule then forbids levels with the same value of λ to cross, but allows crossing of σ states with π states and so on.

Homonuclear molecules

When the nuclei A and B are identical, the system is invariant under reflections about the mid-point of the internuclear line $(\mathbf{R} \to \mathbf{R}, \mathbf{r} \to -\mathbf{r})$. The solutions then divide into even (or gerade) or odd parity (ungerade) classes. In the separated atom limit the even or symmetrical functions are of the form

$$\psi_g \sim \psi_A + \psi_B, \qquad (9-4)$$

and the odd or anti-symmetrical functions are

$$\psi_u \sim \psi_A - \psi_B. \qquad (9-5)$$

In the united atom limit, the wave function has the parity $(-1)^\ell$, so ψ_g is connected to functions with even ℓ, and ψ_u to functions with odd ℓ. The no-crossing rule then forbids the crossing of two even or of two odd levels (see Fig. 9-1).

For the special case of the one electron system the wave equation can be separated and numerical solutions have been obtained for the molecular ions H_2^+ and HHe^{++} (Bates

et al., 1953; Bates and Carson, 1956). The fact that a separation of variables can be made corresponds to an extra hidden symmetry in the one electron problem, and because of this the "no crossing" rule does not always apply in the single electron case. The two lowest electronic states of H_2^+, the hydrogen molecular ion, are designated in the united atom limit as $(1s\sigma_g)$ and $(2p\sigma_u)$. The total interaction energy $\epsilon'(R)$ is shown in Fig. 9-2 for these two states. The ground state of H_2^- is associated with the $(1s\sigma_g)$ potential which provides an attraction, while the $(2p\sigma_u)$ potential is everywhere repulsive. Both states tend asymptotically to $H(1s) + p$ and both are important in the scattering problem.
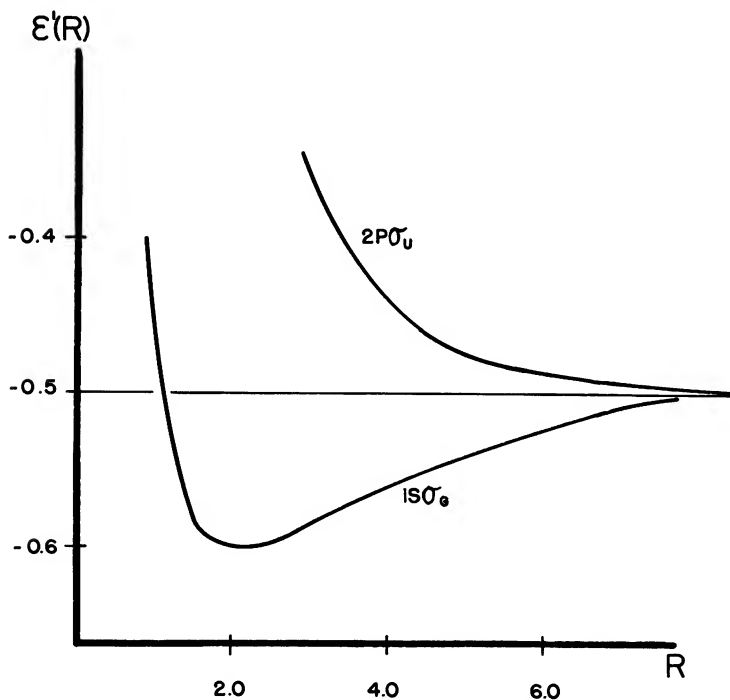
Figure 9-2.   The total interaction energy in the lowest gerade and ungerade states of H_2^+.

The scattering problem

The function χ_n or φ_m required in the scattering problem are defined to have the asymptotic forms (8-37) or (8-38). We may take, then,

$$\chi_n(\mathbf{r}, \mathbf{R}) = \psi_n(\mathbf{r}, \mathbf{R}) \exp(i\ell_1 \mathbf{k}_n \cdot \mathbf{r}_B), \qquad (9\text{-}6)$$

where ψ_n is the molecular orbital, or combination of orbitals, that tends to $\psi_{B_n}(\mathbf{r}_B)$ in the separated atom limits. Were it not for the presence of the exponential factor the matrix elements required would be of simple form, but as we saw earlier it is most important, except at very low velocities, to retain these factors in order to allow for the momentum transfer of the electron in charge exchange. In addition, because the molecular wave functions are quantized with respect to the nuclear axis, the rotation of this axis during the collision leads to strong coupling between states of different magnetic quantum numbers. Fortunately these difficulties do not occur in quite such an acute form in the case of symmetrical resonance in which A and B are identical, and we shall consider this case first.

9-2   SYMMETRICAL RESONANCE COLLISIONS

To illustrate the form of the equations obtained in the case of symmetrical resonance, we shall suppose that the velocity is so low that the exponential factors in (9-6) can be neglected, and that only the two lowest states of each symmetry class (the $1s\sigma_g$ and $2p\sigma_u$) are of importance. If the corresponding wave functions are ψ_g and ψ_u, then asymptotically we have, where ψ_A, ψ_B are atomic wave functions,

$$\psi_g \sim \frac{1}{\sqrt{2}} \left[\psi_A(\mathbf{r}_A) + \psi_B(\mathbf{r}_B) \right] \qquad (9\text{-}7a)$$

$$\psi_u = \frac{1}{\sqrt{2}} \left[\psi_B(\mathbf{r}_B) - \psi_A(\mathbf{r}_A) \right]. \qquad (9\text{-}7b)$$

It follows that

$$\chi(\mathbf{r}, \mathbf{R}) = \frac{1}{\sqrt{2}} (\psi_u + \psi_g), \qquad (9\text{-}8)$$

is the function that is asymptotic to the situation in which the electron is attached to the proton B and

$$\varphi(\mathbf{r},\mathbf{R}) = \frac{1}{\sqrt{2}} \,(\psi_g - \psi_u), \tag{9-9}$$

is asymptotic to the rearranged situation, in which the electron is attached to A. The various matrix elements occurring in the equations (8-49) and (8-51) are then easily evaluated

$$V_{oo} = (\chi, (\overline{H} - E)\chi) = \frac{1}{2}\left[\epsilon_g(R) + \epsilon_u(R)\right] - \epsilon_o \tag{9-10}$$

$$U_{oo} = (\varphi, (\overline{H} - E)\varphi) = \frac{1}{2}\left[\epsilon_g(R) + \epsilon_u(R)\right] - \epsilon_o = V_{oo} \tag{9-11}$$

$$T_{oo} = H_{oo} = \frac{1}{2}\left[\epsilon_g(R) - \epsilon_u(R)\right],$$

where ϵ_o is the ground state energy of the target atom and ϵ_g and ϵ_u are the energies of the molecular ion. Because of the symmetry of the wave functions, all the other matrix elements vanish: $S_{oo} = \Gamma_{oo} = Y_{oo} = 0$. Then we have, with

$$F_o(\mathbf{R}) \simeq A(\mathbf{b}, Z)\, \exp\,(ik_o Z), \quad G_o(\mathbf{R}) \simeq C(\mathbf{b}, Z)\, \exp\,(ik_o Z),$$

that

$$i\,\hbar v\,\frac{\partial A}{\partial Z} = \frac{1}{2}\left\{\epsilon_g(R) - \epsilon_u(R)\right\}C + \frac{1}{2}\left\{\epsilon_g + \epsilon_u - 2\epsilon_o\right\}A \tag{9-12a}$$

$$i\,\hbar v\,\frac{\partial C}{\partial Z} = \frac{1}{2}\left\{\epsilon_g(R) + \epsilon_u(R) - 2\epsilon_o\right\}C + \frac{1}{2}\left\{\epsilon_g - \epsilon_u\right\}A\,. \tag{9-12b}$$

As we expect, from the discussion in the last chapter, the equations decouple; in fact we could have started from the symmetrized expansion

$$\Psi = [F_g(\mathbf{R})\psi_g + F_u(\mathbf{R})\psi_u] \tag{9-13}$$

to obtain the uncoupled equations directly. Defining $A^{\pm}$ as $A^{\pm} = A \pm C$, we find

$$\hbar v i\,\frac{\partial A^+}{\partial Z} = (\epsilon_g - \epsilon_o)A^+ \tag{9-14}$$

$$\hbar v i\,\frac{\partial A^-}{\partial Z} = (\epsilon_u - \epsilon_o)A^-\,.$$

Integrating and combining to form A and C, we find

$$C = \frac{1}{2} \left\{ \exp\left[\frac{1}{\hbar v i} \int_{-\infty}^{\infty} (\epsilon_g - \epsilon_0) dZ\right] - \exp\left[\frac{1}{\hbar v i} \int_{-\infty}^{\infty} (\epsilon_u - \epsilon_0) dZ\right] \right\}$$

(9-15)

and

$$|C|^2 = \sin^2\left[\frac{1}{2\hbar v} \int_{-\infty}^{\infty} (\epsilon_g - \epsilon_u) dZ\right].$$

(9-16)

This expression may be compared with that obtained in the two state atomic expansion (8-93). If ϵ_g and ϵ_u are evaluated using the L.C.A.O. wave functions

$$\psi_{u,g} = \psi_A(\mathbf{r}_A) \pm \psi_B(\mathbf{r}_B)$$

(9-17)

the two expressions coincide (neglecting the transitional exponential factors involving v).

The equations decouple even if the translation factors are not neglected (see Bates and McCarrol, 1962; Bates and Holt, 1966), and we find that

$$|C|^2 = \sin^2\left\{\beta_g^* - \beta_u + \frac{1}{2\hbar v} \int_{-\infty}^{\infty} (\epsilon_g - \epsilon_u) dZ\right\},$$

(9-18)

where β_g and β_u are complicated functions that have the effects of cancelling the integral term at high velocities and thus reducing the cross section.

In the two state approximations, the probability of charge transfer (or elastic scattering) oscillates with unit amplitude for fixed impact parameter as a function of energy. We have already seen that an important source of damping is the coupling to higher electronic states, and that a distinct source of damping arises from the interference between different classical trajectories. This can be seen within the two state approximation (Smith, 1964; Bates and Holt, 1966). The uncoupled equations of motion describe the motion of heavy particles in two distinct potentials, the potentials $\epsilon_g(r)$ and $\epsilon_u(r)$. The semi-classical phase associated with each

trajectory[1] is (in the approximation where we neglect the translational motion of the electron)

$$\chi_g = \frac{1}{\hbar} \int_{-\infty}^{\infty} \frac{1}{v} (\epsilon_g - \epsilon_0) dZ$$

and

$$\chi_u = \frac{1}{\hbar} \int_{-\infty}^{\infty} \frac{1}{v} (\epsilon_u - \epsilon_0) dZ. \tag{9-19}$$

The scattering amplitudes $f(\theta)$ and $g(\theta)$ are then

$$f(\theta) = \frac{1}{2} \left\{ \sqrt{\frac{d\sigma^g}{d\Omega}} \, e^{i\chi_g} + \sqrt{\frac{d\sigma^u}{d\Omega}} \, e^{i\chi_u} \right\}$$

$$g(\theta) = \frac{1}{2} \left\{ \sqrt{\frac{d\sigma^g}{d\Omega}} \, e^{i\chi_g} - \sqrt{\frac{d\sigma^u}{d\Omega}} \, e^{i\chi_u} \right\}, \tag{9-20}$$

where $d\sigma^{g,u}/d\Omega$ are the classical cross sections for scattering in the potential fields ϵ_g and ϵ_u. When these scattering amplitudes differ appreciably, the oscillations in the angular distributions will be damped to a greater or lesser extent. Defining the probability of charge exchange by (8-95) as before, we find

$$P_{CE}(\theta) = \frac{1}{2} \left\{ 1 - g \cos (\chi_g - \chi_u) \right\}, \tag{9-21a}$$

where

$$g = \frac{2 \left(\frac{d\sigma^g}{d\Omega} \right)^{\frac{1}{2}} \left(\frac{d\sigma^u}{d\Omega} \right)^{\frac{1}{2}}}{\left(\frac{d\sigma^g}{d\Omega} + \frac{d\sigma^u}{d\Omega} \right)} \tag{9-21b}$$

---

[1] More exactly we should allow for the difference in v as we transverse each trajectory and use (see (8-55))

$$\chi_{g,u} \simeq \int \left[\left\{ \frac{2\mu}{\hbar^2} (E - \epsilon_{g,u}(R)) \right\}^{1/2} - \sqrt{\frac{2\mu E}{\hbar^2}} \right] dS,$$

where the integration is along the classical path.

If a many-state approximation is used the terms $e^{i\chi_{g,u}}$ must be replaced by a sum of terms $e^{i\chi_g} \rightarrow \sum_j e^{i\chi_g^{(j)}} C_j^{g,u}$, where the $\chi_g^{(j)}$ are appropriate phases arising from each state in the expansion and the $C_j^{g,u}$ are the asymptotic values of the expansion coefficients.

Proton scattering by hydrogen

The two state approximation has been applied to the proton-hydrogen atom system by Dalgarno and Yadav (1953) and Peek (1966), neglecting the translational motion of the electron and by Ferguson (1961) who did not make this approximation. Ferguson used simple analytic forms for $\Psi_{g,u}$ given by Dalgarno and Poots (1954), in atomic units,

$$\Psi_g = N_g \left[e^{-r_A - r_B} + p \left(e^{-r_A} + e^{-r_B} \right) \right] \qquad (9\text{-}22a)$$

$$\Psi_u = N_u \left[(r_A \cos \theta_A - r_B \cos \theta_B) e^{-(r_A + r_B)/2} \right.$$
$$\left. - q \left(e^{-r_A} - e^{-r_B} \right) \right], \qquad (9\text{-}22b)$$

where N_g, N_u are normalization factors and p, q variational parameters. These functions are exact in both the separated and united atom limits and reproduce the energies $\epsilon_{g,u}(R)$ to within 1%.

Ferguson found that when the momentum transfer of the electron was allowed for, the cross section decreased by 5% at 2 kev, by 16% at 5 kev and 45% at 20 kev. Below 2 kev it appears that the translational motion of the electron can be neglected. It does not follow that this is the case when the nuclei A and B are different. In the symmetrical case, charge exchange takes place without an electronic transition, the equations for $F_{g,u}(\mathbf{R})$ being uncoupled, but, in general, charge exchange takes place through the coupling terms $\mathbf{\Gamma}_{nm}$, $\mathbf{\Delta}_{nm}$, etc., that involve the matrix element of the operator $\mathbf{\nabla}_R$ between the different electronic states, and these terms are

sensitive to the exponential momentum transfer factors. Below 20 kev and down to 1 kev, the results of Ferguson agree quite closely with those of McCarrol based on the two state atomic expansion. In particular, the theory fails to predict the oscillations observed in the fixed angle experiments with the correct turning points of damping. This is in part due to the coupling expected between the $2p\sigma$ and $2p\pi$ states because of the rotation of the internuclear line. This coupling is included in a four state approximation in which the $2s\sigma$, $2p\sigma$, $2p\pi$ and $3d\pi$ terms are retained (Bates and Williams, 1964). In this work the turning points agree well with those observed (see Table 9-1), but the amplitude of the oscillations is greater than that shown in the experiments (see Fig. 8-10).

Table 9-1

Turning points of the differential cross section as a function of energy for $H + H^+$ collisions at 3° scattering angle, in kev.

Theory (Bates and Williams, 1964)		Experiment (Lockwood and Everhart, 1962)	
Maximum	Minimum	Maximum	Minimum
0.79		0.78	
	1.09		1.11
1.55		1.57	
	2.33		2.39
3.70		3.92	

In the proton-hydrogen system the further interference effects due to nuclear identity have been discussed by Smith (1967) who shows that these are very small for energies above 15 ev and do not contribute significantly to the observations.

Scattering of helium ions by helium

The angular distribution of the elastic scattering of He^+ by He has been measured in the angular range $0°$ to $36°$ by Lorents and Aberth (1965) at energies from 20 to 600 ev. Fixed angle cross sections have also been measured at higher energies up to 25 kev by Lockwood et al. (1963). In the wide angle scattering data (an example of which is shown in Fig. 9-3), the oscillations observed can be interpreted as being due in the main to interference between the gerade and ungerade states of the He_2^+ molecular ion. In addition at large angles small oscillations are seen superimposed on the main oscillations. These are due to nuclear interference effects,
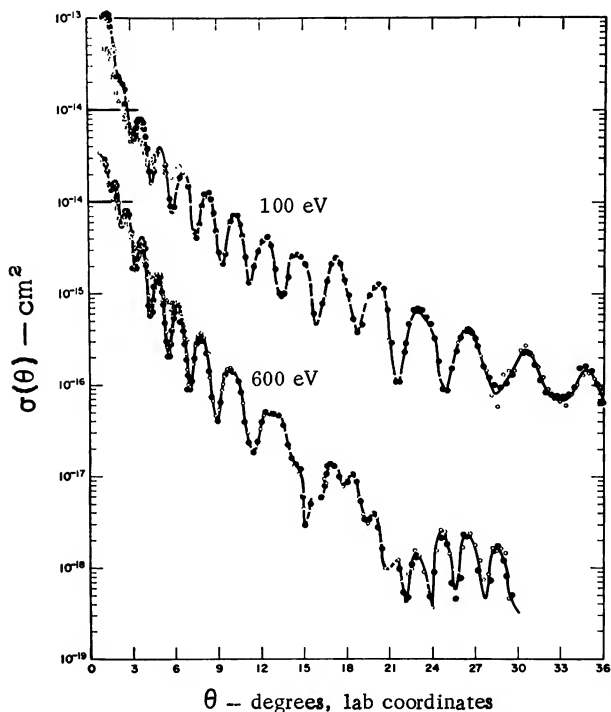
Figure 9-3.   The angular distribution of the elastic scattering of He^+ by He (Lorents and Aberth, 1965).
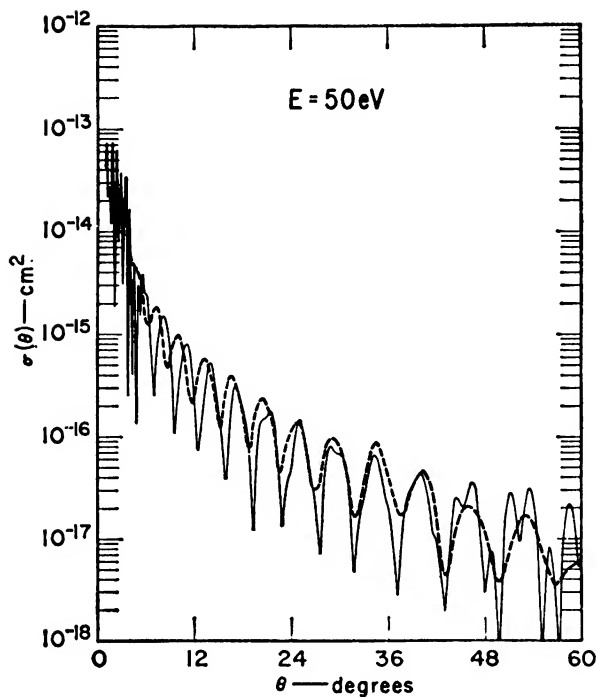
Figure 9-4.   The angular distribution of the elastic scattering of He$^+$ by He.
Experimental data: ----- (Lorents and Aberth, 1965).
Theoretical calculation ——— (Marchi and Smith, 1964).

and this is confirmed by the disappearance of the oscillations
when the experiments are conducted with He^{4+} scattered by
He^3 (Aberth et al., 1965). At the lower energies the sharp
increase in cross section at small angles is attributed to
rainbow scattering (see Chapter 2).

   A theoretical interpretation of these results has been
given by Marchi and Smith (1965). They have determined the
classical cross section and the semi-classical phases for
scattering by the lowest gerade and ungerade potentials for
the He + He$^+$ system. The potentials are shown in Fig. 9-5;
the ungerade potential is related to the configuration
Be$^+$((2s)^{2}2p) in the united atom limit and the gerade potential
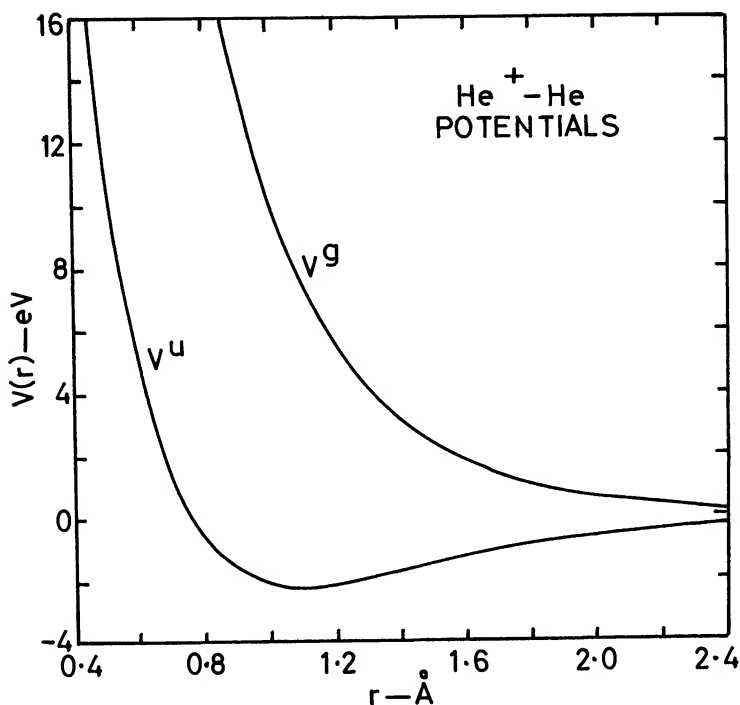
Figure. 9-5. The interaction potential between He$^+$ and He in the lowest gerade and ungerade states.

to Be$^+((1s)(2p)^2)$. It is seen that the ungerade potential has an attractive region and, as we noted in Chapter 2, potentials of this kind always give rise to rainbow scattering and the observed rainbow angle can be satisfactorily explained in this way. The calculated differential cross sections agree rather well with the observations as shown in Fig. 9–4. The differences where they occur are due to the effects of inelastic processes, to describe which requires further terms in the expansion of the wave function. The terms concerned have been discussed by Litchen (1963), who has shown that they are connected with curve crossing in the gerade potential. Smith et al. (1965) have given a qualitative discussion of these inelastic effects and have shown that they can account satisfactorily for most of the anomalies.

Several interesting experiments have been performed in which angular distribution for other charge exchange processes have been measured, but detailed theoretical analysis is for the most part lacking.

9-3   THE LANDAU-ZENER-STÜCKELBERG APPROXIMATION

There is no satisfactory theory of non-resonant charge transfer reactions at low energies, but an indication of the behavior of the cross section for some processes in which curve crossing or pseudo-curve-crossing occurs can be obtained from an approximation of the two state equations due to Landau (1932), Zener (1932) and Stückelberg (1932). Consider once more the transference of an electron from state n of the atom (B + e) to the state m of the atom (A + e). Let $\Psi_n^A(\mathbf{r}, \mathbf{R})$ and $\Psi_m^B(\mathbf{r}, \mathbf{R})$ be molecular orbitals, with total energies $\epsilon_n(R)$, $\epsilon_m(R)$, that are asymptotic to the appropriate atomic states:

$$\Psi_n^A(\mathbf{r}, \mathbf{R}) \to \psi_{B_n}(\mathbf{r}_B),$$

$$\Psi_m^B(\mathbf{r}, \mathbf{R}) \to \psi_{A_m}(\mathbf{r}_A). \tag{9-23}$$

Now suppose the potential curves $\epsilon_n(R)$ and $\epsilon_m(R)$ cross for some value of $R = R_c$, as in Fig. 9-6a.

If the two states have the same symmetry, crossing is in general forbidden. In this case, a better approximation to the molecular wave functions is obtained from a linear combination of Ψ_n and Ψ_m:

$$\varphi_{1,2} = \lambda_{1,2}(R)\Psi_n^A + \mu_{1,2}(R)\Psi_m^B, \tag{9-24}$$

where the parameters $\lambda_{1,2}$, $\mu_{1,2}$ are determined variationally. The new energy curves $E_1(R)$, $E_2(R)$ will then appear to repel each other as in Fig. (9-6b). Let us choose φ_1 to be the combination that approaches Ψ_n^A for large R and φ_2 to approach Ψ_m^B:
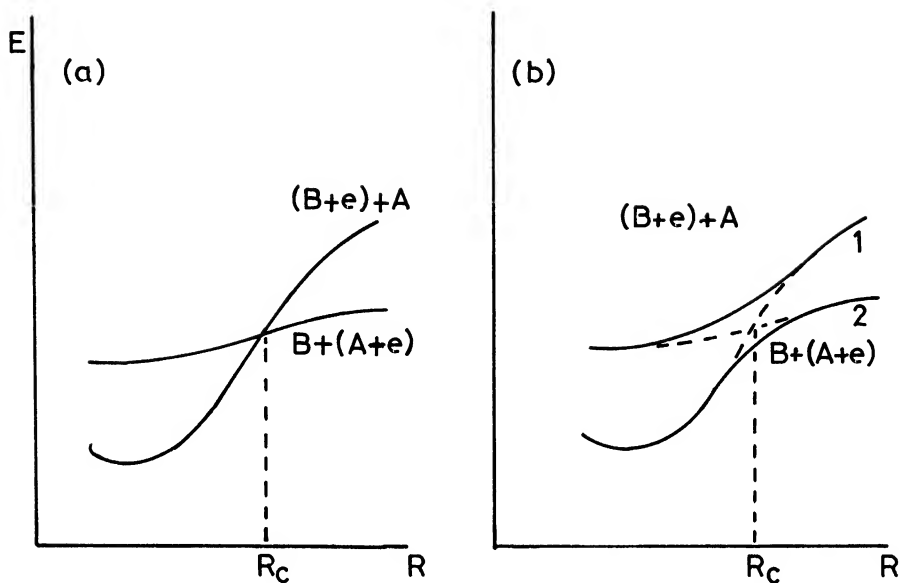
Figure 9-6a, b.   Potential curves illustrating crossing and the Landau-Zener formula.

$$\varphi_1 \rightarrow \Psi_n^A, \quad E_1 \rightarrow \epsilon_{n'}$$

$$\varphi_2 \rightarrow \Psi_m^B, \quad E_2 \rightarrow \epsilon_m. \qquad R \rightarrow \infty \qquad (9\text{-}25)$$

In other words, for $R > R_c$; $\lambda_2 > \mu_2$. Then it can be shown
for $R < R_c$, $\lambda_1 < \mu_1$, $\mu_2 > \lambda_2$, and that φ_1 and φ_2 have
changed in that φ_1 now represents the situation in which e is
attached to A rather than B, and φ_2 the situation in which e
is attached to B rather than A.

The two state approximation can be based on either the

function $\varphi_{1,2}$ or Ψ_n^A, Ψ_m^B. If we are given the function $\varphi_{1,2}$ which represent 'pseudo-crossing' where the potential curves approach but do not cross, we can clearly invert the equation (9-24) and find Ψ_n^A and Ψ_m^B as a linear combination of φ_1 and φ_2. We shall choose to develop the two state approximation in terms of the functions Ψ_n^A, Ψ_m^B that exhibit a real crossing point. Without loss of generality, we can take Ψ_n^A and Ψ_m^B to be orthogonal[2] and normalized. At sufficiently low energies it is supposed that the translational velocity of the electron can be ignored; then the basic equations (8-60a,b) simplify, making the usual impact parameter assumptions to

$$i v \hbar \frac{\partial A}{\partial Z} = \Gamma_{nm} C \exp\left[i \mu(Z) \right] \tag{9-26a}$$

$$i v \hbar \frac{\partial C}{\partial Z} = \Gamma_{mn}^* A \exp\left[-i \mu(Z) \right], \tag{9-26b}$$

where

$$\Gamma_{nm} = 2 \int d\mathbf{r}\, \Psi_n^{A*}(r,R) \frac{\partial}{\partial Z} \Psi_m^B(r,R) \tag{9-27}$$

and

$$\mu(Z) = \frac{1}{\hbar v} \int_{-\infty}^{Z} \left[\epsilon_n(R) - \epsilon_m(R) \right] dZ. \tag{9-28}$$

As usual $R^2 = Z^2 + b^2$, where b is the impact parameter and the matrix elements S, H and T vanish, because of the orthogonality of Ψ_n^A and Ψ_m^B. The boundary conditions are that $A(-\infty) = 1$ and $C(-\infty) = 0$.

Because of the oscillating nature of $\exp\left[\pm i \mu(Z)\right]$, transitions between the states will occur most rapidly at values of R for which μ is small. At the crossing point R_c

---

[2]If the functions are not orthogonal, we may "orthogonalize" them by using Ψ_n^A and $\Psi_m^B - \left(\Psi_n^A, \Psi_m^B \right) \Psi_n^A$ as the required functions.

We have that $\mu(Z_c) = 0$. This suggests that an expansion of the equation is made about the point $R = R_c$. We write

$$\epsilon_n(R) - \epsilon_m(R) = (Z - Z_c)a,$$

and

$$\Gamma_{nm} = \Gamma_{mn}^* = 2\beta, \qquad (9\text{-}29)$$

where a and β are treated as constants. Then combining the two equations we find

$$iv\hbar \frac{\partial^2 C}{\partial Z^2} = \frac{4\beta^2}{iv\hbar} C + \frac{i\beta a}{hv} \frac{\partial C}{\partial Z} (Z - Z_c). \qquad (9\text{-}30)$$

At $Z \to -\infty$, the boundary condition satisfied by $\partial C/\partial Z$ is found from the second of the coupled equations to be

$$\frac{\partial C}{\partial Z} \xrightarrow[Z \to -\infty]{} \frac{2\beta}{i\hbar v} \exp\left[-\frac{iaZ^2}{hv} \right]. \qquad (9\text{-}31)$$

Zener (1932) showed that equation (9-30) can be transformed to Weber's equation, which has a known solution from which it is found that

$$|C(Z = +\infty)|^2 = 1 - e^{-2\gamma}; \quad \gamma = \frac{\pi|\beta|^2}{hv|a|}. \qquad (9\text{-}32)$$

The probability $P = e^{-2\gamma}$ is the chance that the system remains on the curve a in Fig. (9-6a), that is, no transition is made in terms of the basis set Ψ_n^A, Ψ_m^B. Alternatively, referring to Fig. 9-6b, we see that P is the probability that a transition has occurred from curve 1 to curve 2. The system traverses the crossing region twice during the collision, and this must be taken into account. The probability that a transition is made in which the system enters on curve 1, $R > R_c$, remains on curve 1, $R < R_c$, and finally leaves on curve 2 is $P(1 - P)$, while the probability that the system enters on curve 1, $R > R_c$, makes a transition to curve 2, $R < R_c$, and finally remains on curve 2, $R > R_c$ is also $P(1 - P)$. The total probability that a transition has occurred is thus

$$P_{21} = 2P(1 - P). \qquad (9\text{-}33)$$

This is a function of the impact parameter b, and the cross section is, in the usual way,

$$\sigma_{2 \to 1} = 2\pi \int_0^\infty b P_{21}(b) \, db. \qquad (9\text{-}34)$$

It has been pointed out by Bates (1960) that this simple approximation must fail in many circumstances. For example, we have already noted that because of the rotation of the inter-nuclear line, there is strong coupling between states of different magnetic quantum number and the two state approxi-mation can only be used for transition between σ states. Moreover, the region from which transitions may be expected to occur rapidly can be estimated. If this region has width ΔZ and it is assumed that the transitions are important if $\mu'(z)$ charges by $\sim\pi$ as Z varies between $Z_c + \Delta Z$ and $Z_c - \Delta Z$, then

$$\frac{1}{v\hbar} \left| \int_{Z_c - \Delta Z/2}^{Z_c} \left(\epsilon_n(R) - \epsilon_m(R)\right) dZ + \int_{Z_c}^{Z_c + \Delta Z/2} \left(\epsilon_n(R) - \epsilon_m(R)\right) dZ \right| \simeq \pi.$$

$$(9\text{-}35)$$

This equation is satisfied when

$$\Delta Z = \sqrt{\frac{4\pi v\hbar}{a}} \ .$$

The transition region is unbounded as v increases, and be-cause of this the Landau formulae lead to an inverse variation of the cross section with velocity; however, the cross section found from the exact solution of the coupled equation is propor-tional to $1/v^2$ for large v. (In both cases the important effect of the translational motion of the electron has been ignored.) A more serious objection is that even at low velocities ΔZ can be of the order Z_c which destroys the basis of the approximation, which assumes that the region over which transitions occur is narrow.

Despite these difficulties the Landau-Zener approxi-mation has been used to discuss a variety of reactions. Particularly favorable cases arise for exothermic reactions such as

$$A + B^{++} \to A^+ + B^+ + \text{kinetic energy} \qquad (9\text{-}36)$$

or endothermic reactions such as

$$A + B \rightarrow A^+ + B^- - \text{kinetic energy}. \qquad (9\text{-}37)$$
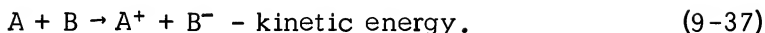
In such cases, the crossing point is controlled by the long range forces and occurs at large atomic separations where the L.C.A.O. (linear combination of atomic orbitals) wave functions can be used. In the first case, the interaction in the initial state is attractive because of the $1/R^4$ polarization potential between a charge and a neutral system (see Chapter 5), while in the final state the interaction is proportional to $1/R$ and is repulsive. In the second example, the final state interaction is strongly attractive, like $1/R$, and in the initial state the interaction is the Van der Waals polarization potential which behaves like $1/R^6$.

Some examples for which numerical calculations have been made are (Bates and Moiseiwitsch, 1954)

$$H + Be^{++} \rightarrow H^+ + Be^+$$
$$H + Si^{++} \rightarrow H^+ + Si^+ \qquad (9\text{-}38)$$
$$H + Mg^{++} \rightarrow H^+ + Mg^+$$

and (Dalgarno, 1954)

$$H + Al^{+++} \rightarrow H^+ + Al^{++} (^2S \text{ and } ^2P)$$
$$H + B^{++} \rightarrow H^+ + B^+ (^1P)$$
$$H + Li^{++} \rightarrow H^+ + Li^+ (^3S \text{ and } ^1P) \qquad (9\text{-}39)$$
$$H + Al^{++} \rightarrow H^+ + Al^+.$$
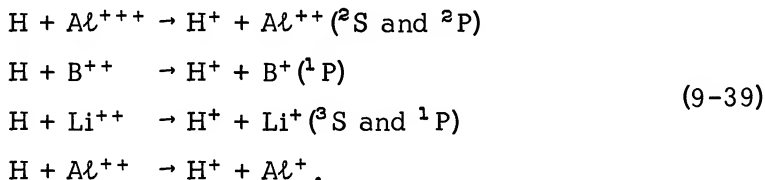
These processes involve the transfer of an electron from an orbital around one passive closed core to an orbital around another, and can be treated as one-electron problems. The crossing points are determined by the charges and polarizabilities of the ions and occur at large distances of separation; for example, in the second group of reactions, at 3.34, 6.58, 11.1, 8.80, 20.9 and 5.29 atomic units respectively.

Improvements to the Landau–Zener approximation, for charge exchange, in which the oscillations observed at fixed impact parameter can be accounted for, have been discussed by Litchen (1965).

9-4   SLOW ELASTIC COLLISIONS

While the differential cross section for elastic or
charge exchange scattering may exhibit an oscillatory be-
havior, the total elastic cross section at low, but not too low,
energies is accurately given by applying the classical theory
to the average effective potential between the atoms or ions.
At thermal energies, the collisions are so slow that only the
long range part of the potential will influence the cross sec-
tion, while at higher energies, the potential may be represen-
ted as the sum of the long range terms and parameterised short
range terms. Much effort has gone into the determination of
effective inter-atomic forces by analysing the total elastic
cross sections, which for many processes have been measured
as a function of energy from a few electron volts to a few kev.
This work has been reviewed in detail by Mason and Vander-
slice (1962) and we will not discuss it here.

The long range part of the potential can be discussed
by perturbation theory or by using variational methods, in the
same general way that the long range $1/r^4$ potential was
determined in Chapter 5. The leading term in the potential
between neutral systems behaves like $1/R^6$ and arises because
both systems may be polarized, and to the lowest order the
interaction is of dipole-dipole form. The elementary theory of
the Van der Waal's interaction is reviewed in most books on
quantum mechanics (see for example, Landau and Lifshitz,
1959), and we will not repeat the discussion here. A recent
comprehensive review of the methods of calculating the co-
efficients in the expansion of the long range interaction in
powers of $1/R$,

$$V(R) = -\sum_{\ell=1}^{\infty} \sum_{L=1}^{\infty} \frac{C(\ell, L)}{R^{2(\ell+L+1)}} \qquad (9-40)$$

has been given by Dalgarno (1966). The higher terms in this
expansion arise from dipole-quadrupole, quadrupole-quadrupole
interactions and so on. The coefficients $C(\ell, L)$ have been
calculated for a wide variety of systems, including hydrogen
with inert gases, alkali metal with inert gases, and inert gases
with inert gases.

Departures from the $1/R^6$ variation of the potential can occur in
cases of degeneracy, for example in collisions between atoms of the

same species, one of which is in an excited state and one in an unexcited state. As in the case of electron scattering near a degenerate threshold, the degeneracy has the effect of increasing the range of the potential. If the excited state and the ground state are connected with an optically allowed transition, then the potential behaves like $1/R^3$ and in general if the transition connecting the two states is governed by a multipole of order ℓ then the potential varies like $1/R^{2\ell+1}$, unless both the excited and unexcited states are S-states, in which case as usual, the interaction decays exponentially.

We shall consider two examples of transitions that at low velocities take place through the long range part of the interaction; both are of astrophysical importance.

Transitions in the total angular momentum of an atom

During a slow collision, transitions can occur between states of an atom that differ only in the total angular momentum j, for example the reaction

$$H + 0(^3P_{j=2}) \rightarrow H + 0(^3P_{j=1,0}) \qquad (9-41)$$
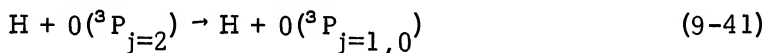
which is an important source of cooling in interstellar space, and has been investigated by Callaway and Dugan (1967). The four oxygen electrons in s-states can be ignored and the interaction arises between the hydrogen atom and the four p-state electrons. The long range van der Waal interaction is

$$V_{eff} = \sum_i v_i(x_i), \qquad (9-42)$$

where the sum is over the coordinates of the four p-electrons and

$$v(x_i) = -\frac{1}{2} \frac{ae^2 r_i^2}{R^6} (3 \cos^2 \theta_i + 1). \qquad (9-43)$$

In this expression a is the polarizability of atomic hydrogen. The time-dependent equations coupling the j = 2 and the j = 0 and 1 states can be written down and they were solved approximately using a method, due to Callaway and Bauer (1965), that insures unitarity (see also Callaway and Bartling, 1966). Similar calculations were carried out for hydrogen-carbon interactions.

Spin transitions

A similar process, that occurs mainly through the long range interactions at low velocities, is spin exchange. The total spin F of a hydrogen atom can be either $F = 1$ (triplet) or $F = 0$ (singlet) and transitions between these states can occur during collisions with other atoms. Spin exchange in collisions between hydrogen atoms provide a cooling mechanism of importance in astrophysical contexts (Purcell and Field, 1956). At low velocities, the interaction between two hydrogen atoms can be described in terms of the $^1\Sigma_g$ and $^3\Sigma_u$ electronic states of H_2, where the superscripts refer to the total spin states of the two electrons, which can be singlet or triplet. The associated interaction energies $^{1,3}V(R)$ have been calculated accurately by Dalgarno and Lynn (1956) using second order perturbation theory; $^{1,3}V(R) \simeq 13/R^6$ (atomic units) for large R. Although asymptotically $^1V(R)$ approaches $^3V(R)$, at small R the two functions are different, in fact

$$^3V(R) - {}^1V(R) = 3.435\ R^2\ e^{-1.974\ R}.$$

The wave function $^{1,3}F(\mathbf{R})$ describing the relative motion of the two atoms satisfies

$$\{\nabla^2 + [k^2 - {}^{1,3}V(R)]\}^{1,3}F(\mathbf{R}) = 0, \tag{9-44}$$

where

$$^{1,3}F(\mathbf{R}) \sim \exp(i\mathbf{k} \cdot \mathbf{R}) + R^{-1}\ {}^{1,3}f(\theta)\exp(ikR).$$

Labeling the two protons A and B, and ignoring their identity, we can consider states in which proton A has a spin wave function $\alpha(A)$ and proton B has spin function $\chi(B)$, where χ can be either α or β. The complete wave function for the singlet and triplet electron states is, including spin functions, asymptotically

$$\Psi^1 \sim [\exp(i\mathbf{k} \cdot \mathbf{R}) + R^{-1}\ {}^1f(\theta)\exp(ikR)]\,\alpha(A)\chi(B) \times$$

$$\times \frac{1}{\sqrt{2}}\ [\alpha(1)\beta(2) - \beta(1)\alpha(2)],$$

where $\alpha(i)$, $\beta(i)$, $i = 1,2$ are the electron spin functions.

$$\Psi^3 \sim [\exp (i\mathbf{k} \cdot \mathbf{R}) + R^{-1} \; {}^3f(\theta) \exp (ikR)] a(A)\chi (B) \times$$

$$\times \frac{1}{\sqrt{2}} [a(1)\beta (2) + \beta (1)a(2)]. \qquad (9\text{-}45)$$

where in the second line the Z component of the total electron spin S_z had been taken to be zero. As S_z is a constant of the motion, we do not have to consider the other members of the triplet multiplet with spin functions $a(1)a(2)$ and $\beta (1)\beta (2)$, which cannot couple to cause spin exchange, in the approximation in which nuclear exchange is ignored.

Consider an initial state in which the hydrogen atom A has spin $F = 1$, with Z component $M = 1$. The spin wave function of the atom A is then $a(A)a(1)$ and corresponds to the wave function $(\Psi^1 + \Psi^3)$; in fact

$$\Psi^1 + \Psi^3 \sim \frac{2}{\sqrt{2}} \exp (i\mathbf{k} \cdot \mathbf{R})[a(A)a(1)\chi (B)\beta (2)]$$

$$+ R^{-1} \exp (ikR) \frac{1}{\sqrt{2}} a(A)a(1)\chi (B)\beta (2)[{}^1f(\theta) + {}^3f(\theta)] +$$

$$+ \left\{ \left[\frac{1}{2\sqrt{2}} (a(A)\beta (1) + \beta (A)a(1)) + \frac{1}{2\sqrt{2}} (a(A)\beta (1) - \right. \right.$$

$$\left. \left. - \beta (A)a(1)) \right] \right\} \chi (B)a(2) [{}^3f(\theta) - {}^1f(\theta)]. \qquad (9\text{-}46)$$

The scattered wave contains three terms, the first two of which correspond to the state with $F = 1$ and the last to $F = 0$. The cross section for the transitions from $F = 1$ to $F = 0$ is then determined by the amplitude (normalizing to an incident wave of unit amplitude)

$$g(F = 1 \rightarrow F = 0) = \frac{1}{2\sqrt{2}} \{{}^3f(\theta) - {}^1f(\theta)\}. \qquad (9\text{-}47)$$

Expanding in phase shifts ${}^{1,3}\delta_\ell$

$$g(\theta) = \frac{1}{4ik\sqrt{2}} \sum_{\ell=0}^{\infty} \left[e^{2i \; {}^3\delta_\ell} - e^{2i \; {}^1\delta_\ell} \right] (2\ell + 1)P_\ell (\cos \theta), \qquad (9\text{-}48)$$

and the total cross section is

$$\sigma(F = 1 \to F = 0) = \sum_{\ell=0}^{\infty} \frac{\pi}{2k^2} (2\ell + 1) \sin^2 ({}^3\delta_\ell - {}^1\delta_\ell).$$

(9-49)

The phase shifts ${}^3\delta_\ell$, ${}^1\delta_\ell$ were calculated by Dalgarno and Henry (1964) from the radial equations (atomic units),

$$\frac{d^2}{dR^2} [{}^{1,3}g_\ell(R)] + \left[k^2 - {}^{1,3}V(R) - \frac{\ell(\ell + 1)}{R^2} \right] {}^{1,3}g_\ell(R) = 0$$

(9-50)

and their results are shown in Fig. 9-7 for energies between threshold and 20×10^{-3} ev. The maximum at 0.005 ev is due to $({}^3\delta_\ell - {}^1\delta_\ell)$ passing through $\pi/2$ at this energy for certain ℓ values.

The impact parameter version of the cross section formula (9-49) is interesting (Dalgarno, 1961). It is

$$\sigma(F = 1 \to F = 0) = \frac{\pi}{2} \int_0^\infty b \sin^2 \Gamma(b) \, db$$
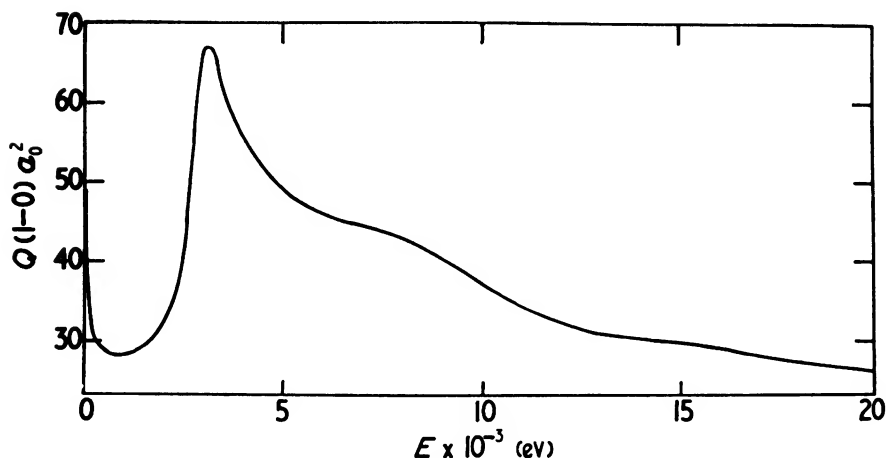
Figure 9-7. The spin exchange cross section for scattering of hydrogen atoms by hydrogen atoms (Dalgarno and Henry, 1964).

where

$$\Gamma(b) = \frac{M}{mk} \int_b^\infty \frac{^3V(R) - {}^1V(R)}{(1 - b^2/R^2)^{1/2}} \, dR.$$

Smith (1966) has considered the effects of nuclear exchange, using the J.W.K.B. method to determine the phase shifts. The amplitude for spin exchange in this case is obtained by replacing $^1f(\theta)$ and $^3f(\theta)$ by $[{}^{1,3}f(\theta) - {}^{1,3}f(\pi - \theta)]$. The exchange effects can be considerable for H-H scattering, but in proton-hydrogen scattering the exchange effects cancel.

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Chapter 10

ELECTRON SCATTERING
BY MOLECULES

The scattering of electrons or atoms by molecules presents a theoretical problem of considerably greater complexity than those we have already considered, because the scattering amplitude can depend on the orientation of the molecule and because of the extra rotational and vibrational degrees of freedom involved. At low velocities the interaction between a molecule. and other systems is often governed mainly by the long range polarization forces which can be calculated from perturbation theory. We shall not discuss all such processes here, but we shall examine some of the methods that have been used to discuss the scattering of electrons by diatomic molecules, making no attempt at completeness.[1] Most detailed calculations have been carried out for scattering by the hydrogen molecular ion and for the neutral hydrogen molecule which serve as prototypes for electron-molecule collisions in the same way as the scattering of electrons by hydrogen and helium atoms serves as a prototype of electron-atomic collisions.

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[1] A comprehensive review of earlier work on electron-molecule collisions has been given by Craggs and Massey (1959).

10-1   MOLECULAR WAVE FUNCTIONS

The fundamental approximation in molecular physics has already been discussed in earlier chapters, where it was explained that, to first order in (m/M), the ratio of the mass of the electron to that of the nuclei, the electrons can be considered as moving in the field of the stationary nuclei. As before, the complete Hamiltonian is divided by writing

$$H = - \frac{\hbar^2}{2\mu} \nabla_R^2 + \bar{H}, \tag{10-1}$$

where μ is the reduced mass of the two nuclei A and B and $\mathbf{R}$ is the internuclear line. The electronic wave functions and energies are then defined by

$$\{\bar{H}(R, \mathbf{r'}) - \epsilon_n(R)\}\psi_{n,\Lambda}(R, \mathbf{r'}) = 0, \tag{10-2}$$

where R enters as a parameter and $\mathbf{r'}$ stands for the coordinates of all the electrons collectively, in a frame of reference moving with the molecule with the Z' axis along the internuclear line. The component of the total orbital angular momentum of the electrons, along the nuclear axis, is Λ and the terms with $\Lambda = 0, 1, 2$ are denoted by Σ, Π and Δ as before. Each electronic state is characterized by the total spin S and the terms can be designated as $^{(2S+1)}\Sigma, \ ^{(2S+1)}\Pi \ \ldots$. In addition to invariance under rotations about the internuclear axis, the system is invariant under reflections in any plane passing through the axis of the molecule. Such reflection changes the sign of the component of the angular momentum along the internuclear axis so that, as we have already remarked, the state with non-zero values of Λ are doubly degenerate. In the case of Σ states such a reflection can only alter the wave function by a constant c, whose square is unity since a double reflection restores the original situation. Taking c to be real we must have either $c = +1$ or $c = -1$ and there are two distinct states, for one of which the wave function changes sign under reflection and for one of which the wave function is unaltered under reflection. These states are denoted by Σ^- and Σ^+ respectively. When the molecule consists of two nuclei having the same charge, the electronic wave functions divide into even and odd classes under reflection about the mid-point of the internuclear line, as discussed in Chapter 9,

giving rise to the additional classification of gerade (even) and ungerade (odd) states.

The exact wave function can be expanded in the form (in what follows we shall suppress the spin variables)

$$\Psi(\mathbf{r},\mathbf{R}) = \sum_n \psi_{n,\Lambda}(R,\mathbf{r}')P_{n,\Lambda}(\mathbf{R}) \qquad (10\text{-}3)$$

where the wave functions $P_{n,\Lambda}(\mathbf{R})$ representing the nuclear motion satisfy coupled equations similar to those of (8-49). As the coupling between the different electronic states arises from matrix elements like $\hbar^2/2M(\psi_n,\nabla_R^2\psi_m)$ and $\hbar^2/M(\psi_n,\nabla_R\psi_m)$, which are of order (m/M), for most purposes a single term in the expansion represents a good approximation.

In obtaining the equation of motion for the functions $P_{n,\Lambda}(\mathbf{R})$, it should be remembered that the differential operations ∇_R and ∇_R^2 must be carried out for fixed $\mathbf{r}$, where $\mathbf{r}$ represents the position vector of the electron defined in a reference system fixed in space. If the rotating frame of reference has cartesian axes (x',y',z'), with z' along the internuclear axis, and the fixed frame of reference, with the same origin, has axes (x,y,z), then the rotation that brings the (x',y',z') axes into the (x,y,z) axis can be defined by Euler angles (α,β,γ), where the rotation is carried out in the following order:

(a)   a rotation through an angle α about the z' axis;
(b)   a rotation through an angle β about the new y axis;
(c)   a rotation through an angle γ about the new z axis.

The polar coordinates (Θ,Φ) of $\mathbf{R}$ with respect to the fixed frame of reference are then identical with the Euler angles (β,γ). The relationship between (x,y,z) and (x',y',z') is

$$x = x'(\cos\alpha\cos\gamma - \cos\beta\sin\alpha\sin\gamma) -$$
$$- y'(\sin\alpha\cos\gamma + \cos\beta\cos\alpha\sin\gamma) +$$
$$+ z'\sin\beta\sin\gamma$$
$$y = x'(\cos\alpha\sin\gamma + \cos\beta\sin\alpha\sin\gamma) -$$
$$- y'(\sin\alpha\sin\gamma - \cos\beta\cos\alpha\cos\gamma) -$$
$$- z'\sin\beta\cos\gamma,$$

$$z = x' \sin \beta \sin \alpha + y' \sin \beta \cos \alpha + z' \cos \gamma. \quad (10\text{-}4)$$

Using these relations the wave equation satisfied by $P_{n,\Lambda}(\mathbf{R})$ can be obtained.[2] Neglecting the electron spin and small terms of order (m/M), it is found that $P_{n,\Lambda}(\mathbf{R})$ is the product of a radial function $p_{n,\Lambda,j}(R)$ and an eigenfunction of J^2 and $J_z, Q_{\Lambda,j,m}$, where $\mathbf{J}$ is the orbital angular momentum of the system,[3,4]

$$P_{n,\Lambda}(\mathbf{R}) = R^{-1} p_{n,\Lambda,j}(R) Q_{\Lambda,j,m}(\beta,\gamma). \quad (10\text{-}5)$$

As usual, $j(j + 1)\hbar^2$ and $m\hbar$ are the eigenvalues of J^2 and J_z respectively. The radial functions satisfy the equation

$$\left\{ + \frac{\hbar^2}{2\mu} \left(\frac{d^2}{dr^2} - \frac{j(j+1) - \lambda^2}{R^2} \right) + E - \epsilon_{n,\Lambda}(R) \right\} p_{n,\Lambda,j}(R) = 0.$$
$$(10\text{-}6)$$

If the interaction energy $\epsilon(R)$ possesses a minimum at a value of R as in Fig. 10-1, curve (a), a stable molecular state is possible, and the electronic state is said to be attractive. The nuclear motion in this state will be confined to the potential well, the penetration of the wave function into the potential barrier being very small. If the interaction energy

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[2] A full account of the structure of diatomic molecules has been given by Herzberg (1939).

[3] The functions $Q_{\Lambda,j,m}(\beta,\gamma)$ reduce to the ordinary spherical harmonics $Y_{j,m}(\beta,\gamma)$ if $\Lambda = 0$. For $\Lambda \neq 0$, they are related to the rotation matrices $D^j(\alpha,\beta,\gamma)$; see Edmonds (1960).

[4] The total orbital angular momentum $\mathbf{J}$ is the sum of $\mathbf{L}_e$ and $\mathbf{L}_n$, where $\mathbf{L}_e$ is the angular momentum of the electrons and $\mathbf{L}_n$ that of the nuclei. As $\mathbf{L}_n$ is in a direction at right angles to the internuclear line, the component of $\mathbf{J}$ along the internuclear line is equal to Λ, the component of $\mathbf{L}_e$ in the same direction. It follows that $j \geq \Lambda$.

$\epsilon(R)$ does not possess a minimum, as in curve (b), the mole-
cule is unstable and will dissociate. In both cases, for large
R, $\epsilon(R)$ will tend to the sum of the energies of the separated
atoms. The equilibrium position of the molecule is at the
internuclear separation R_0, where R_0 is the root of

$$\frac{\partial \epsilon(R)}{\partial R} = 0.$$
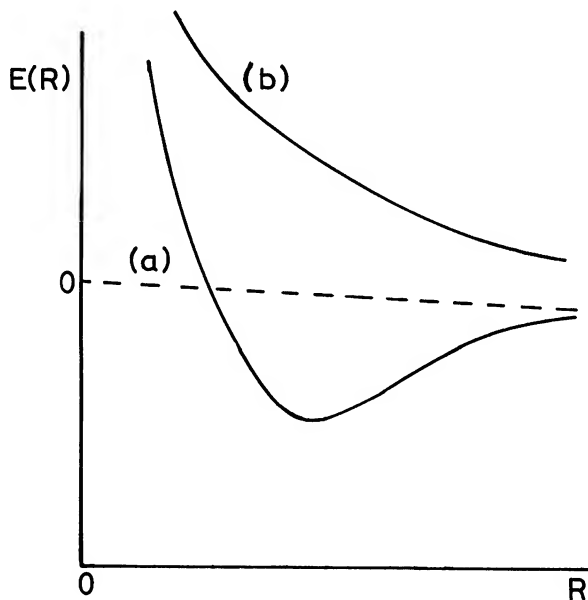
Figure 10-1.   The electronic energy $\epsilon(R)$ of a diatomic molecule as a function of
the internuclear distance R. If the molecule is stable $\epsilon(R)$ possesses a minimum
(curve a). If $\epsilon(R)$ does not possess a minimum the molecule will dissociate (wave b).

We shall refer to $\epsilon(R_0)$ as the electronic energy of the molecule, to

$$\frac{\hbar^2}{2\mu}\left[\frac{j(j+1)-\lambda^2}{R_0^2}\right]$$

as the rotational energy, and to

$$-\frac{\hbar^2}{2\mu}\left[\frac{j(j+1)-\lambda^2}{R_0^2}\right] - \epsilon(R_0) = E_\nu, \tag{10-7}$$

as the vibrational energy. The eigenvalues E_ν can be obtained by expanding $\epsilon(R)$ about the equilibrium position, in the lowest approximation E_ν is the energy of a one dimensional oscillator, and

$$E_\nu = \hbar\omega\left(\nu + \frac{1}{2}\right), \quad \nu = 0,1,2,\ldots, \tag{10-8}$$

with $\quad \mu\omega^2 = 2\left(\dfrac{\partial^2 \epsilon(R)}{\partial R^2}\right)_{R=R_0}$.

More accurate values can be obtained from numerical solutions of the radial wave equation.

The electronic energy of the diatomic molecule is of the order of a few electron volts, for example in the ground state of molecular hydrogen $\epsilon(R_0) = 4.7$ ev. This may be compared with the vibrational energy which is proportional to $1/\sqrt{\mu}$, and is an order of magnitude smaller and the rotational energy which is proportional to $1/\mu$ and is smaller still. For hydrogen, the vibrational energy is determined by $\hbar\omega$ which has the value 0.54 ev, and the rotational energy by $(\hbar^2/2\mu R_0^2)$ which has the value 7.6×10^{-3} ev. Thus the vibrational levels split the electronic levels into levels lying close together compared with the spacing of the electronic levels themselves, and the rotational motion causes a further fine splitting of the vibrational levels. As the characteristic times associated with the electronic, vibrational and rotational motions are of the order $\hbar/\epsilon(R_0)$, $1/\omega$ and $2\mu R_0^2/\hbar$ respectively, it is seen that the Born–Oppenheimer approximation in which the nuclei are treated as stationary for the purpose of calculating the electronic wave functions is usually completely justified.

The electronic wave functions

To be useful in a practical calculation of a scattering cross section, reasonably simple approximations to the electronic wave functions must be employed. These functions can be classified as single centered or two centered according to whether they are explicit functions of $\mathbf{r}_i$, the position vector of the ith electron with respect to the center of mass of the nuclei or of $(\mathbf{r}_{iA}, \mathbf{r}_{iB})$ the position vectors of the ith electron with the nuclei A and B. In the former representation it is easy to obtain the correct wave function in the united atom limit, while in the latter the separated atom limit arises naturally.

Single center wave functions

As an example of the construction of a single center wave function, we may consider the case of the hydrogen molecular ion H_2^+. In the united atom limit, the ground state of H_2^+ goes over into the 1s state of the helium ion He^+. This suggests that a single variational approximation to the $(1s\sigma_g)$ state of H_2^+ would be

$$\Psi_g(\mathbf{r},\mathbf{R}) = \sqrt{\frac{Z^3}{\pi}}\; e^{-Zr}, \qquad (10\text{-}9)$$

where $\mathbf{r}$ is measured from the mid-point of the internuclear line and $Z(R)$ is a variational parameter which is a function of R, such that as $R \to 0$, $Z(R) \to 2$, the charge on the helium nucleus. As the lowest ungerade state in the united atom limit is the $(2p)$ level of the helium, the $(1s\sigma_u)$ level of H_2^+ (designated $(2p\sigma_u)$ in the united atom limit) might be represented as

$$\Psi_u(\mathbf{r},\mathbf{R}) = \sqrt{\frac{Z^5}{32\pi}}\; r \cos\Theta\, e^{-Zr/2}. \qquad (10\text{-}10)$$

More elaborate trial functions can be formed by taking linear combinations of functions of this hydrogenic type, or of some members of some other complete set. For instance Hagstrom and Shull (1959) have used combinations of the functions $f_{n,\ell,m}(\mathbf{r})$, where

$$f_{n,\ell,m}(\mathbf{r}) = R_{n\ell}(2Zr)Y_{\ell,m}(\Theta,\varphi), \qquad (10\text{-}11)$$

and

$$R_{n\ell}(2Zr) = (2Z)^{3/2} \{n(n + \ell + 1)!\}^{-3/2} \{(n - \ell - 1)!\}^{1/2} \times$$

$$\times (2Zr)^{\ell} L^{2\ell+2}_{n-\ell+1}(2Zr) e^{-Zr} \quad n \geq \ell - 1. \qquad (10\text{-}12)$$
$$|m| \leq \ell$$

This set is both orthonormal and discrete. For a many electron diatomic molecule, the wave function can be built up from correctly symmetrized products of these one electron functions. The orbital molecular wave function possesses cusps at the position of the nuclei A and B, and (except for R = 0) it is difficult to represent these discontinuities using single centered wave functions, and this is one of the reasons why expansions based on such wave functions are in general rather slowly convergent. For excited states the method is very successful, because the mean radius of the charge distribution is greater than the internuclear separation and the further the electron is from the center of the molecule, the more the two nuclei look like a single charge at the center of the molecule.

A different kind of single center wave function, that represents the cusps at A and B in a natural manner is due to Temkin (1963). Taking the midpoint of AB as origin, the electronic wave function for H_2 satisfies the Schrödinger equation (atomic units),

$$\left[-\frac{1}{2}\nabla_r^2 - \frac{1}{|\mathbf{r} + \mathbf{R}/2|} - \frac{1}{|\mathbf{r} - \mathbf{R}/2|} + \frac{1}{R} - \epsilon(R) \right]\Psi(\mathbf{r},\mathbf{R}) = 0.$$
$$(10\text{-}13)$$

On expanding the potential in terms of the angle between $\mathbf{r}$ and $\mathbf{R}$, this becomes

$$\left[-\frac{1}{2}\nabla_r^2 - \sum_{\ell}' V_{\ell}(r,R)P_{\ell}(\cos\Theta) + \frac{1}{R} - \epsilon(R) \right]\Psi(\mathbf{r},\mathbf{R}) = 0,$$
$$(10\text{-}14)$$

where the prime denotes that the sum is over even values of ℓ only. The wave functions of either symmetry can also be expanded in terms of spherical harmonics, taking $\mathbf{R}$ as the axis we have that

$$\psi_g^{\lambda}(\mathbf{r},\mathbf{R}) = \sum_n' \frac{\varphi_n^{\lambda}(r,R)}{r} Y_{n,\lambda}(\Theta,\varphi),$$

$$\psi_u^{\lambda}(\mathbf{r},\mathbf{R}) = \sum_n{}'' \frac{\varphi_n^{\lambda}(r,R)}{r} \, Y_{n,\lambda}(\Theta,\varphi),\tag{10-15}$$

where the single and double primes denote sums over even and odd values of n respectively. The radial functions then satisfy, using (10-14),

$$\left(\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2} + \epsilon(R) - \frac{2}{R}\right)\varphi_{\ell}^{\lambda}(r,R) +$$

$$+ 2\sqrt{\frac{4\pi}{2\ell+1}} \sum_L{}' \sum_n V_L(r,R) C_{\ell L n}^{\lambda 0 \lambda} \varphi_n^{\lambda}(r,R) = 0,$$

$$\tag{10-16}$$

where

$$C_{\ell L n}^{\lambda 0 \lambda} = \int Y_{\ell,\lambda}^{*} Y_{L,0} Y_{n,\lambda} d\Omega$$

$$\tag{10-17}$$

$$= \left[\frac{(2\ell+1)(2L+1)}{4\pi(2n+1)}\right]^{1/2} C_{\ell L}(n,0,0,0) C_{\ell L}(n,0,\lambda,-\lambda)$$

In the lowest order approximation, the $(1s\sigma_g)$ ground state of H_2^+ is represented by φ_0^0 which satisfies

$$\left[\frac{d^2}{dr^2} + \frac{6}{R} + \epsilon\right]\varphi_0^0 = 0, \quad 2r < R,$$

$$\tag{10-18}$$

$$\left[\frac{d^2}{dr^2} + \frac{4}{r} - \frac{2}{R} + \epsilon\right]\varphi_0^0 = 0, \quad 2r > R.$$

The change in form of the equation at $r = R/2$ allows the correct representation of the cusps at these points. The function φ_1^0 similarly represents the lowest order approximation to $(1s\sigma_u)$. This method is capable of producing accurate wave functions even when a few terms in the expansion are taken.[5] In fact a single term is often sufficient.

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[5] For an application to $(HeH)^{++}$, see Rabinovitch (1965).

Two center wave functions

In the separated atom limit, the wave functions for H_2^+ must become equal to the wave function of a hydrogen atom, centered either on proton A or on proton B. The lowest order wave functions for the $(1s\sigma_{u,g})$ states could be represented by the simple variational forms

$$\psi_{g,u}(\mathbf{r},\mathbf{R}) = \frac{1}{\sqrt{2}} \left\{ \varphi_{1s}(Z,r_A) \pm \varphi_{1s}(Z,r_B) \right\}, \qquad (10\text{-}19)$$

where $\varphi_{1s}(Z,r)$ is a hydrogenic function

$$\varphi_{1s}(Z,r) = \sqrt{\frac{Z^3}{\pi}} \; e^{-Zr}, \qquad (10\text{-}20)$$

and the variational parameter $Z(R)$ is such that as $R \to \infty$, $Z(R) \to 1$. Clearly better approximations are obtained by taking sums of terms of this general type.

For many electron atoms there are two ways of building up a suitable wave function. We may take products of functions, each of which describe the motion of a single electron in the field of the two nuclei and this is known as the molecular orbital method. For example, the wave function for the neutral hydrogen molecule could be written as

$$\psi(\mathbf{r}_i,\mathbf{R}) = \chi(\mathbf{r}_1)\chi(\mathbf{r}_2)\sigma(12), \qquad (10\text{-}21)$$

where $\mathbf{r}_i$ is the position vector of the ith electron from the center of mass, $\sigma(12)$ is a spin function and $\chi(\mathbf{r})$ is a molecular orbital, which can be represented as in equation $(10\text{-}19)$

$$\chi_{g,u}(\mathbf{r}_i) = \frac{1}{\sqrt{2}} \left\{ \varphi_{1s}(Z,r_{iA}) \pm \varphi_{1s}(Z,r_{iB}) \right\}. \qquad (10\text{-}22)$$

Alternatively, we may start from the separated atom limit. In the case of molecular hydrogen the wave function at large R becomes equal to the product of two hydrogen wave functions, and an approximation to the lowest states is

$$\psi_{g,u}(\mathbf{r}_1,\mathbf{r}_2;\ \mathbf{R}) = \frac{1}{\sqrt{2}} N_{g,u}(R) \left[\varphi_{1s}(Z,r_{1A})\varphi_{1s}(Z,r_{2B}) \pm \right.$$
$$\left. \pm \varphi_{1s}(Z,r_{2A})\varphi_{1s}(Z,r_{1B}) \right] \sigma^{\mp}(12), \qquad (10\text{-}23)$$

where the upper signs correspond to the gerade (g) and the lower to the ungerade (u) states. Because of the Pauli principle the lowest g state is a singlet, $^1\Sigma_g$, and the spin function $\sigma^-(12)$ is

$$\sigma^-(1,2) = \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)], \qquad (10\text{-}24)$$

and the lowest u state is the triplet, $^3\Sigma_u$,

$$\sigma^+(1,2) = \begin{cases} \alpha(1)\alpha(2), \\ \dfrac{1}{\sqrt{2}}\big(\alpha(1)\beta(2) + \beta(1)\alpha(2)\big), \\ \beta(1)\beta(2). \end{cases} \qquad (10\text{-}25)$$

The factor $N_{g,u}(R)$ is a normalization factor determined by the equation

$$(N_{g,u}(R))^{-2} = 1 \pm \int \varphi_{1s}(r_{1A})\varphi_{1s}(r_{2B})\, d\mathbf{r}. \qquad (10\text{-}26)$$

In the molecular orbital approximation there are different methods of combining the single electron orbitals $\chi_{g,u}$ with the correct symmetry. For example, the lowest states of H_2 are

$$\psi_g^1 = \chi_g(\mathbf{r}_1)\chi_g(\mathbf{r}_2)\sigma^-(1,2),$$
$$\psi_g^2 = \chi_u(\mathbf{r}_1)\chi_u(\mathbf{r}_2)\sigma^-(1,2),$$
$$\psi_u^1 = \big[\chi_g(\mathbf{r}_1)\chi_u(\mathbf{r}_2) - \chi_g(\mathbf{r}_2)\chi_u(\mathbf{r}_1)\big]\sigma^+(1,2), \qquad (10\text{-}27)$$
$$\psi_u^2 = \big[\chi_g(\mathbf{r}_1)\chi_u(\mathbf{r}_2) + \chi_g(\mathbf{r}_2)\chi_u(\mathbf{r}_1)\big]\sigma^-(1,2).$$

Each of these configurations corresponds to a different energy, with ψ_g^1 corresponding to the lowest $^1\Sigma_g^+$ state.

As in problems concerning atomic structure, in place of single electron functions depending on variational parameters, wave functions of the self consistent field type can be calculated. The equation for a single electron moving in the field of two fixed centers can be separated in elliptic coordinates (λ,μ,φ) where

$$\lambda = \frac{r_A + r_B}{R} \, , \, \mu = \frac{r_A - r_B}{R} \qquad (10\text{-}28)$$

and φ is the azimuthal angle of the plane containing $\mathbf{r}_A$ and $\mathbf{r}_B$, and for H_2^+ the wave functions $\psi = F(\lambda)G(\mu)\Phi(\varphi)$ are known exactly (Bates et al., 1953). Potential energy curves for the systems in which we are most interested, H_2 and H_2^+, are shown in Figs. 10-2 and 10-3.
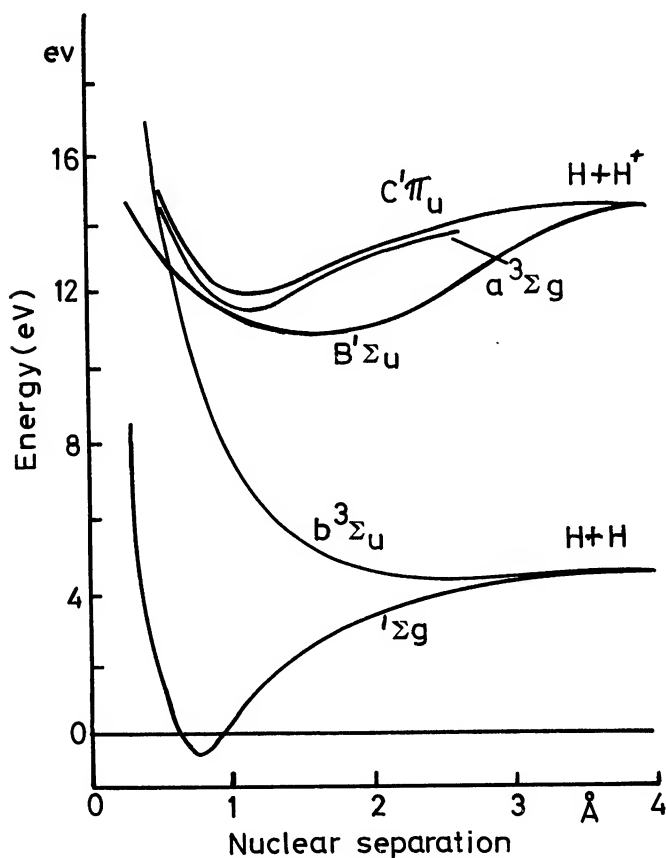
Figure 10-2. Potential energy curves for hydrogen.
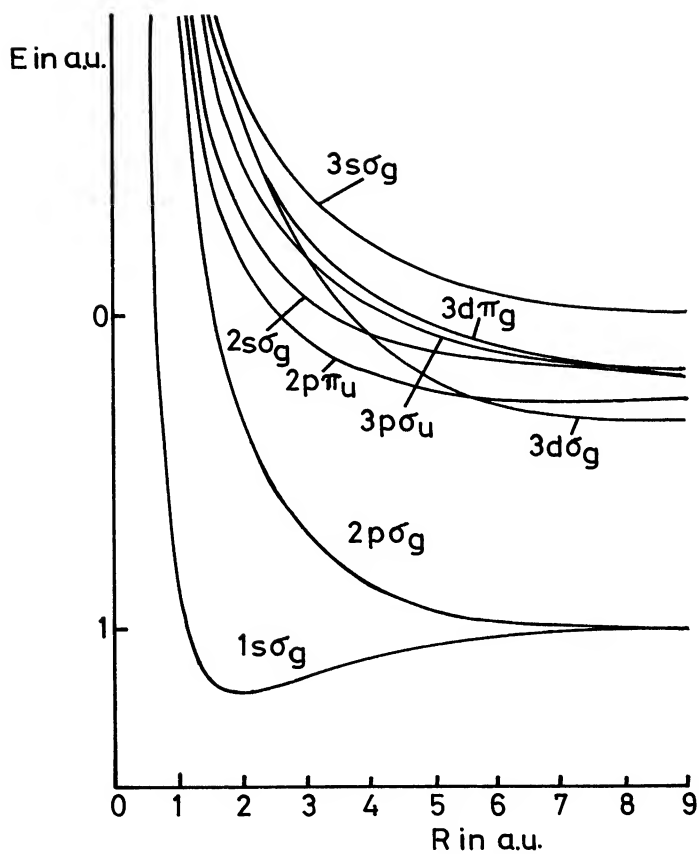
Figure 10-3.   Potential energy curves for the hydrogen molecular ion.

10-2   HIGH ENERGY SCATTERING: THE BORN AND OCHKUR APPROXIMATIONS

The internal state of a diatomic molecule is specified by the electronic configuration n, the vibrational quantum number ν and the angular momentum quantum numbers j, Λ as well as the spin s. An electron of sufficient energy may excite the molecule to a state specified by the set of quantum numbers (n',ν',j',Λ',s') or be scattered elastically.

When the velocity of the incident electron is greater than the velocity of the target electron it is reasonable to use Born's approximation to calculate the cross section for a given excitation or elastic scattering process. In the high velocity region exchange effects will be unimportant, with the exception of transitions in which the spin of the target changes. that   take place entirely through electron exchange. The rotational motion of the nuclei is so slow compared with the electronic motion that in calculating electronic excitation rates, the internuclear line can be considered to be in a fixed direction in space (Θ,Φ), and the differential cross section for an electronic transition summed over all final rotational states is obtained simply by averaging over all orientations of the internuclear line. This will be shown in the context of the Born approximation, but is correct in general. Some general statements can also be made about the final vibrational states of importance in excitation. The electronic transitions are fast compared with the vibrational motion of the nuclei, and may be considered to take place at a fixed value of **R**. For example in Fig. 10-4 curves (a) and (b) represent the interaction energy in two electronic states. The vibrational motion of the nuclei is such that the wave function is small beyond the classical turning points. If these are R_1 and R_2, centered about the equilibrium position R_0, then the probability of finding the value of R outside the region $R_1 < R < R_2$ is small. The transitions from the state (a) to the state (b) will take place with an appreciable probability only within this range of values of R, and the final vibrational states of importance will be those which have classical turning points in the same interval. This is known as the Frank-Condon principle. If the interaction curve is attractive, as in Fig. 10-4(A), the vibrational levels excited will be bounded, but if the curve is repulsive as in Fig. 10-4(B), the
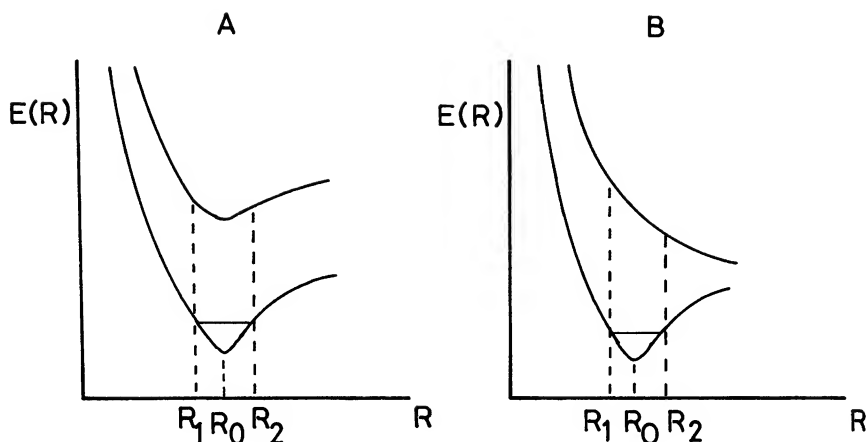
Figure 10-4.   The Frank-Condon principle.

nuclear motion will be unbounded and the molecule will dis-
sociate. Various other possibilities exist; for example, the
state represented by the upper curve may be subject to auto-
ionization and the transition proceeds in the two steps:—

$$e + (AB) \rightarrow (AB)^* + e$$

$$\rightarrow A + B^+ + 2e. \tag{10-29}$$

The scattering amplitude for a transition from the state
$i \equiv (n, \nu, j, \Lambda)$ to the state $f \equiv (n', \nu', j', \Lambda')$ can be written
down just as for electron-atom scattering, and (atomic units)

$$-2\pi f_{fi}(\theta, \varphi) = \int d\mathbf{x} \int d\mathbf{R} \int d\tau \psi_{n'}^*(\mathbf{r}, \mathbf{R}) P_{\nu'}^*(R) Q_{j',m'}^*(\Theta, \Phi) e^{-i\mathbf{k}_f \cdot \mathbf{x}} \times$$

$$\times \left[\frac{Z_A}{r_A} - \frac{Z_B}{r_B} + \sum_i \frac{1}{|\mathbf{x} - \mathbf{r}_i|} \right] \psi_n(\mathbf{r}, \mathbf{R}) P_\nu(R) Q_{j,m}(\Theta, \Phi) e^{+i\mathbf{k}_i \cdot \mathbf{x}}, \tag{10.30}$$

where $\int d\tau$ denotes integration over the coordinates $\mathbf{r}_i$ of all the molecular electrons, $\mathbf{x}$ is the position vector of the incident electron with respect to the center of mass of the heavy particles A and B, where $\mathbf{r}_A$ and $\mathbf{r}_B$ are the distance of the incident electron to A and B respectively. The other symbols have their usual meaning. The terms in Z_A/r_A and Z_B/r_B only contribute to elastic scattering and for inelastic scattering the amplitude can be written as

$$f_{fi}(\theta,\varphi) = \int d\mathbf{R}\, M(\mathbf{R})\left\{P^*_{\nu'}(R)P_\nu(R)\right\}\left\{Q^*_{j',m'}(\Theta,\Phi)\right.$$
$$\left. Q_{j,m}(\Theta,\Phi)\right\}, \tag{10-31}$$

where

$$M(\mathbf{R}) = -\frac{2}{K^2}\int d\tau \psi^*_{n'}(\mathbf{r},\mathbf{R})\psi_n(\mathbf{r},\mathbf{R})\sum_i \exp\,(i\mathbf{K}\cdot\mathbf{r}_i) \tag{10-32}$$

and we have made use of (6-23) to perform the integration over $\mathbf{x}$. The momentum transfer $\mathbf{K}$ is as usual defined as $\mathbf{K} = \mathbf{k}_f - \mathbf{k}_i$.

As a rule, the experiments refer to excitation cross sections summed over all final rotational states. This sum can be performed if it is remembered that the energy separation of the rotational states is very small compared with that of the electronic and vibrational states, so that to a good approximation $M(R,\Theta,\Phi)$ and $P_{\nu'}(R)$ are independent of j' and m'. We can then use the closure property of the $Q_{j',m'}$ to obtain

$$\sum_{j',m'}|f_{fi}(\theta,\varphi)|^2 = \int d\Omega(\Theta,\Phi)\left| \int_0^\infty P_\nu(R)P^*_{\nu'}(R)M(\mathbf{R})Q_{j,m}(\Theta,\Phi)\right.$$
$$\left. R^2\, dR\right|^2. \tag{10-33}$$

In exactly the same way, if we neglect the dependence of $\mathbf{k}_f$ on the final vibrational level, the sum over all final vibrational states can be performed, using the closure property of $P_\nu(R)$. Then for an initial spherically symmetrical rotational state,

$$Q_{j,m} = \frac{1}{\sqrt{4\pi}}$$

and

$$\sum_{j',m',\nu'} |f_{fi}(\theta,\varphi)|^2 = \frac{1}{4\pi} \int d\mathbf{R} \, |P_\nu(R)|^2 \, |M(\mathbf{R})|^2 \quad (10\text{-}34)$$

$M(\mathbf{R})$ is the scattering amplitude for excitation at final orientation (Θ, Φ) of the internuclear line and is a slowly varying function of R compared with the function $P_\nu(R)$. The total cross section for excitation of the level n', summed over all final states of nuclear motion is then

$$\sigma_{n'n} = \frac{k_f}{4\pi k_i} \int_{-1}^{+1} d\cos\Theta \int_0^{2\pi} d\varphi \int R^2 \, dR \, |P_\nu(R)|^2 \, |M(\mathbf{R})|^2.$$

$$(10\text{-}35)$$

This result expresses the approximation that was discussed a little earlier, that is, the cross section can be calculated for a fixed orientation of the internuclear axis and subsequently averaged over all values of $\cos\Theta$ and Φ.

Excitation of H_2^+

Extensive calculations of the excitation of H_2^+ by electron impact have been carried out by Peek (1964, 1965, 1967), who has also considered the cases of excitation by proton and hydrogen atom impact.[6] The important transitions are from the ground state $(1s\sigma_g)$ to the excited states $(2p\sigma_u)$, $(2p\pi_u)$ and $(2s\sigma_g)$, where we have used the united atom designations. The strongest transition is to the $(2p\sigma_u)$ state, which becomes equal to $(1s\sigma_u)$ in the separated atom limit. As this state is repulsive, the excitation represents the dissociative process

$$e + H_2^+(1s\sigma_g) \rightarrow e + H_2^+(2p\sigma_u)$$

$$(10\text{-}36)$$

$$\rightarrow e + H(1s) + p.$$

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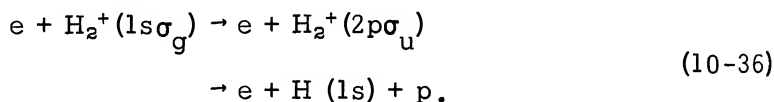
[6] See also Ivash (1958), Kerner (1953) and Bates and Holt (1965).

In this work, Peek used the exact electronic wave functions of H_2^+ calculated by Bates et al. (1953). The L.C.A.O. approximation was employed in the earlier work of Ivash (1953) and where comparison is possible agreement was obtained to within 20%, suggesting that the approximate wave functions may be good enough for most purposes. Writing the cross section arising from the initial vibrational state ν as σ_ν, where

$$\sigma_\nu = \int_0^\infty \sigma(R) |P_\nu(R)|^2 R^2 \, dR, \qquad (10\text{-}37)$$

and

$$\sigma(R) = \frac{k_f}{4\pi k_i} \int_{-1}^{+1} d\cos\theta \int_0^{2\pi} d\varphi \int d\Omega\,(\hat{R}) |M(\mathbf{R})|^2. \qquad (10\text{-}38)$$

The behavior of $\sigma(R)$ as a function of R and σ_ν as a function of ν can be studied. In Table 10-1, $\sigma(R)$ is shown for the equilibrium value $R_0 = 2.0$ and for the values of R near the classical turning points. It is seen that the variation of $\sigma(R)$

Table 10-1

Cross section for the $(1s\sigma_g) \rightarrow (2p\sigma_u)$ excitation of H_2^+ (Peek, 1964)

(Atomic units)

	(a)			(b)	
E(ev)	$\sigma(R=1.4)$	$\sigma(R=2.0)$	$\sigma(R=3.2)$	σ_0	σ_3
50	0.426	0.977	3.25	1.09	1.92
100	0.384	0.635	1.92	0.698	1.17
200	0.197	0.396	1.11	0.431	0.691
300	0.148	0.295	0.745	0.320	0.502
400	0.120	0.230	0.612	0.248	0.383

(a) $\sigma(R)$ — For definition see text.

(b) σ_ν — Cross-section for excitation in which the final vibration state is ν.
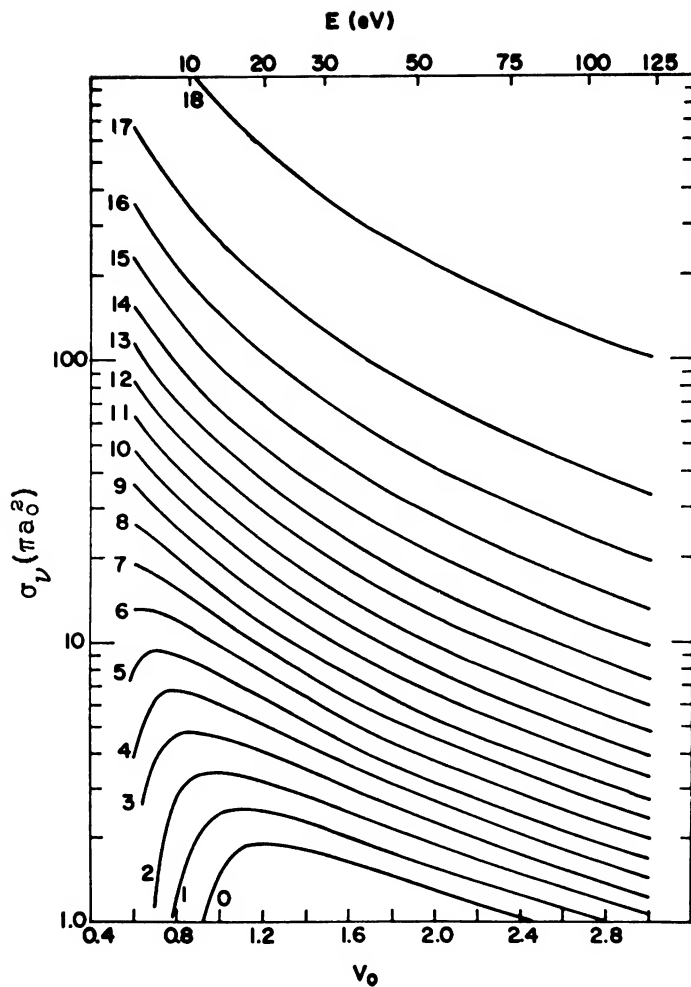
Figure 10-5. The cross sections σ_{ν} for an electron exciting the transition $1s\sigma_g \rightarrow 2p\sigma_u$ in H_2^+, for all 19 bound vibrational states of the ground state of H_2^+. The lower scale is the relative velocity and the upper is the electron energy. The level $2p\sigma_u$ lies in the continuum so the process is dissociative. (Peek, 1964, 1965, 1967.)

with R is important and it is not sufficient to evaluate $\sigma(R)$ at $R = R_0$ and treat it as a constant. The corresponding values of σ_ν are shown for $\nu = 0$ and $\nu = 3$. The cross section increases sharply with increasing ν, and this is shown particularly well in Fig. 10-5, where σ_ν is shown as a function of incident energies for all nineteen bound vibrational states associated with the lowest electronic state of H_2^+.

These results may be compared with measurements by Dunn and Van Zyl[7] (1967). If in the experiment each vibrational level of the $(1s\sigma_g)$ state of H_2^+ is populated by a fraction n_ν of the total number of ions in the $(1s\sigma_g)$ level, the measured cross section is

$$\sigma = \sum_\nu n_\nu \left(\sigma_\nu(2p\sigma_u) + \sigma_\nu(2s\sigma_g) \right) + \bar{\sigma}, \qquad (10\text{-}39)$$

where $\bar{\sigma}$ represents the cross section for excitation and ionization in all other levels. $\bar{\sigma}$ has been estimated using a closure approximation by Peek (1967). Remarkable agreement has been obtained between the calculated cross section and the measurements, illustrated in Fig. 10-6. The measurements which were carried out for energies from 10 to 150 ev, fitted the empirical formulae

$$\sigma = \frac{1}{E} (217 \log_{10}E - 184)\pi, \qquad (10\text{-}40)$$

where σ is atomic units and E is in electron volts, showing the characteristic $(\log(E)/E)$ asymptotic behavior of a dipole transition.

The calculations for proton impact show that, as expected, at high velocities the electron and proton cross section are the same at the same relative velocity. At lower velocities the proton is more efficient than the electron in dissociating the molecule because a greater range of momentum transfers, $(K_{max} - K_{min})$, is allowed.

Electron scattering by H_2

The interaction energy curves of some low lying states of H_2 have been shown in Fig. 10-3. The ground state is a singlet state $^1\Sigma_g^+$ in which both electrons are in the united atom configurations $(1s\sigma_g)$ tending in the separated

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[7]Other measurements of the dissociation cross section have been reported by Dance et al. (1967), which are in essential agreement with those of Dunn and Van Zyl.
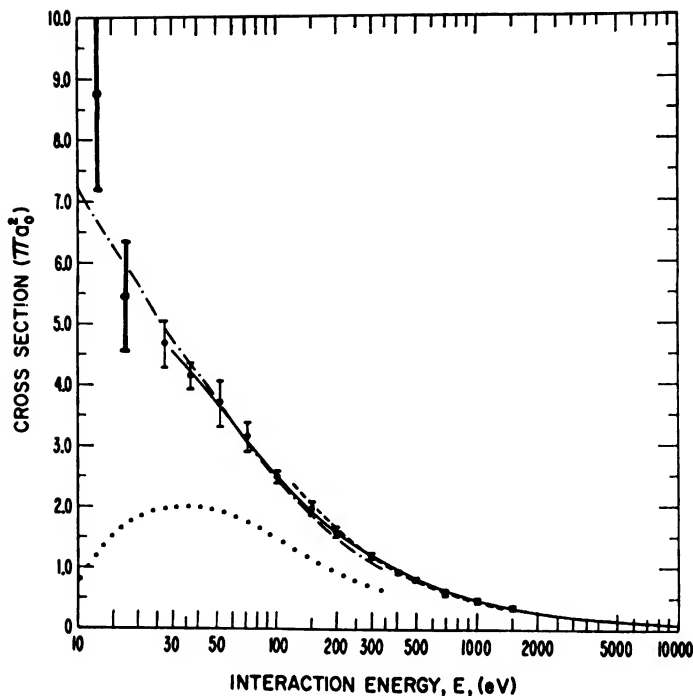
Figure 10-6. The cross section for the dissociation of H_2^+ by electron impact, averaged over vibrational levels.

I	Experimental Data (Dunn and Van Zyl, 1968).
-.-.-	Calculated cross section (Peek, 1966).
.....	Calculated cross section for dissociation from the lowest vibrational state of the ground state (Peek, 1966).

atom limit to two hydrogen atoms in the ground state. The H_2 molecule is stable against dissociation into two hydrogen atoms by 4.4 ev. Two ground state hydrogen atoms can also be brought together in the triplet spin state. In this case, the interaction is repulsive so the $^3\Sigma_u^+$ state of H_2 is unstable. Next come the states that correspond to $H(1s) + H(n = 2)$ in the separated atom limit; these are the $^1\Sigma_n^+$, $^1\Pi_n$ and $^1\Sigma_g^+$ states, designated the B, C and E states respectively. Above the lowest triplet state, $^3\Sigma_u^+$ (designated b) lies the $^3\Sigma_g^+$ (designated a) which is attractive. The correlations for these

Table 10-2

Correlations for H_2

United atom	Term	Separated atom
He(^{1}S, 1s, 1s)	$X^1\Sigma_g^+$	H(1s) + H(1s)
He(2^3P, 1s, 2p)	$b^3\Sigma_u^+$	H(1s) + H(1s)
He(3^1P, 1s, 3p)	$B^1\Sigma_u^+$	H(1s) + H(2s)
He($2\,^3$S, 1s, 2s)	$a^3\Sigma_g^+$	H(1s) + H(2s)
He($2\,^1$P, 1s, 2p)	$C^1\pi_u$	H(1s) + H(2p)
He($2\,^1$S, 1s, 2s)	$E^1\Sigma_g^+$	H(1s) + H(2s)

states are shown in Table 10-2.

    Both elastic scattering by the ground state and the excitation of the ground state to the low lying singlet state have been discussed within the Born approximation. In the early work of Massey and Mohr (1932), exchange effects were computed using the plane wave or Born-Oppenheimer approxima- tion. As we saw earlier, this approximation is not as a rule reliable and in the more recent work of Khare and Moiseiwitsch (1965, 1966) the first order exchange method was used to cal- culate the exchange scattering amplitude. Comparison with the experimental measurements of the elastic scattering differ- ential cross section (Webb, 1935) is made difficult because of doubts about the normalization of the experiments, but Khare and Moisewitsch concluded that the Born approximation was reliable at electron impact energies in excess of 100 ev.

    As an alternative to the first order exchange method, the Ochkur or the Ochkur-Rudge approximations to the exchange amplitude may be investigated. As in the case of scattering by atoms, the exchange amplitude in the Ochkur approximation is given in terms of the direct amplitude by the simple expression

$$g_{fi} = \frac{K^2}{2k_i^2} f_{fi}.$$ (10-41)

Khare (1966a,b) has estimated the cross section for excitation to the B, C and D states in this approximation using single centered wave functions for the states of H_2 (see Huzenaga, 1957). In this work it has been assumed that $\sigma(R)$, defined by (10.38), can be treated as a constant and evaluated at the equilibrium separation of the nuclei $R = R_0$. In this case, the dependence of the cross section on the initial vibrational state is removed since

$$\int_0^\infty |P_\nu(R)|^2 R^2 \, dR = 1.$$ (10-42)

The differential cross section for unit momentum transfer is then, in the Ochkur approximation,

$$\frac{d\sigma}{dK} = \left(\frac{K}{2k_i^2}\right) \int d\Omega(\hat{R}) |M(\mathbf{R})|^2 \left(1 - \frac{K^2}{2k_i^2}\right)^2.$$ (10-43)

It may be noted that as in the case of scattering by atoms, a generalized oscillator strength may be defined as

$$F_{fi}(K) = \frac{1}{4}(k_f^2 - k_i^2)K^2 \left(\frac{d\sigma}{dK}\right).$$ (10-44)

The general behavior of the excitation cross section for the B and C states, is to rise steeply from threshold (11.4 and 12.4 ev respectively) to a maximum near 50 ev. It is only in the vicinity and below this maximum that exchange effects are important. Near the maximum these effects reduce the cross section by 8-10%. In the energy range up to 300 ev, these calculations agree well with earlier work by Roscoe (1941), who used a two centered wave function for the hydrogen molecule.

Some comparison with experiment is possible for the sum of the B and C state excitation cross section at 25 kev. Fig. 10-7 shows that at this energy the agreement between theoretical results of Roscoe and of Khare with the measurements of Greider (1964) is quite good. At these energies, the Born approximation should certainly be accurate and the results are a test of the molecular wave function employed.
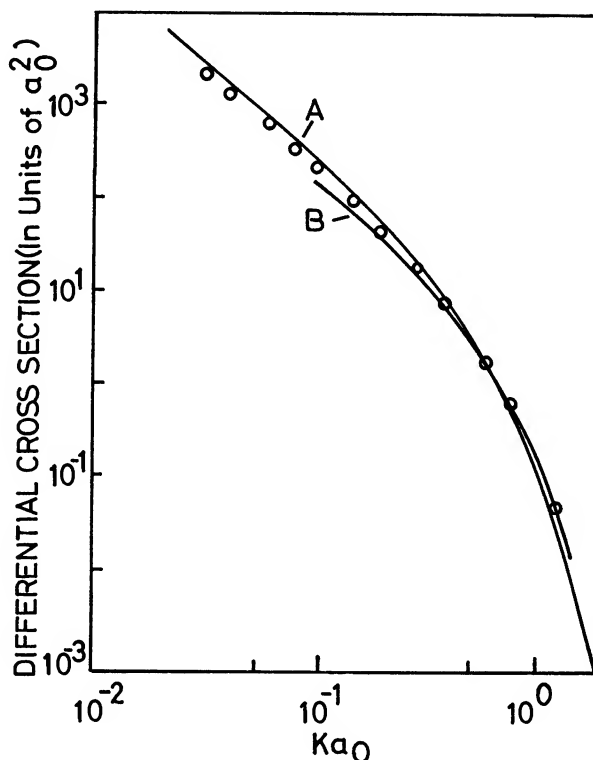
Figure 10-7. Excitation of the sum of the B and C states of hydrogen.
00000   Experimental cross section (Grieder, 1964).
━━━━ A, B   Calculated cross section in the Born approximation (Roscoe, 1944; Khare, 1966).

Excitation of the triplet states has also received a good deal of attention (Khare, 1967; Cartwright et al., 1967). As this process can only occur through exchange, the results depend critically on the approximation used to estimate the exchange amplitude. Cartwright et al. show that there are considerable differences between the cross sections calculated in the Ochkur approximation and in Rudge's modification of the Ochkur approximation and also that the results are sensitive to the details of the assumed ground state H_2 wave function.

An impulse approximation

When the wave length of the incident electron is small compared with the internuclear distance, the molecule will tend to behave like two independent atomic scattering centers.

The scattering amplitude can then be expanded in multiple scattering series in which each term describes a succession of scatterings at each center. In the lowest approximation, which is akin to the impulse approximation, the scattering amplitude can be represented as a sum of the scattering amplitudes from each atom in the molecule, weighted by suitable phase factors that allow for the displacement of each atom from the center of mass of the molecule. If the position vector of each atom in the molecule, with respect to the center of mass, is $\mathbf{r}_i$, then the outgoing spherical wave arising from elastic scattering at the ith atom from an incident plane wave $\exp(i\mathbf{k}\cdot\mathbf{x})$ is

$$f_i(\theta)\,\frac{e^{ik|\mathbf{x}-\mathbf{r}_i|}}{|\mathbf{x}-\mathbf{r}_i|}\,e^{i\mathbf{k}\cdot\mathbf{r}_i}, \tag{10-45}$$

where $f_i(\theta)$ is the scattering amplitude proper to the atom i. The factor $e^{i\mathbf{k}\cdot\mathbf{r}_i}$ allows for difference in phase of the incident wave between the center of mass and the scattering center. For large $|\mathbf{x}|$, this becomes

$$\left[f_i(\theta)\,e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}_i}\right]\frac{e^{ikx}}{x}, \tag{10-46}$$

where $\mathbf{k}'$ is the final momentum of the scattered electron ($|k'|=|k|$).

The differential cross section for scattering from the molecule is then

$$\frac{d\sigma}{d\Omega}=\left|\sum_i e^{i\mathbf{K}\cdot\mathbf{r}_i}f_i(\theta)\right|^2 \tag{10-47}$$

$$=\sum_{ij}f_i^*(\theta)f_j(\theta)\,\exp\,i\mathbf{K}\cdot(\mathbf{r}_i-\mathbf{r}_j),$$

for a diatomic molecule. Averaging over all orientations of the internuclear axis

$$\left\langle\frac{d\sigma}{d\Omega}\right\rangle_{av}=\frac{1}{4\pi}\int\sum_{ij}f_i^*(\theta)f_j(\theta)\,\exp\left(i\mathbf{K}\cdot(\mathbf{r}_i-\mathbf{r}_j)\right)d\Omega(\hat{\mathbf{K}}) \tag{10-48}$$

$$=\sum_{ij}f_i^*(\theta)f_j(\theta)\,\frac{\sin K|\mathbf{r}_i-\mathbf{r}_j|}{K|\mathbf{r}_i-\mathbf{r}_j|}.$$

When both atoms are identical we have that

$$\left\langle\frac{d\sigma}{d\Omega}\right\rangle_{av} = 2\left(\frac{d\sigma}{d\Omega}\right)^A \left(1 + \frac{\sin KR_0}{KR_0}\right),$$

where $(d\sigma/d\Omega)^A$ is the cross section for scattering from each atom alone. The most important correction to this formula will arise from double scattering in which the electron scatters first from one and then from the other atom. There is some evidence that this is small at high energies (Hoerni, 1956). Bullard and Massey (1933) discussed the scattering of electrons by nitrogen in this way for energies between 30 and 780 ev, and fair agreement with the observed angular distribution was obtained. Further work along these lines has been reviewed by Craggs and Massey (1959).

10-3   LOW ENERGY SCATTERING

Very few detailed calculations of elastic scattering or electronic excitation have been carried out at low energies, where Born's approximation is inappropriate. Stier (1932) and later Fisk (1936, 1937) have analyzed the scattering data from a number of homonuclear molecules in terms of an effective (optical model) potential for which a parametric form was assumed, the parameter being chosen to fit the data. The first calculations based on molecular wave functions and allowing for exchange were by Massey and Ridley (1956), who treated the case of electron scattering by the ground state of hydrogen. They assumed a molecular wave function of the self consistent field type given by Carlson (1938) and expressed the wave function in the form (for s wave scattering)

$$\Psi(\mathbf{x}, \mathbf{r}_1, \mathbf{r}_2, \mathbf{R}) = AF(\mathbf{x})\Psi_H(\mathbf{r}_1, \mathbf{r}_2, \mathbf{R})\sigma(1,2,3), \quad (10\text{-}49)$$

where Ψ_H is the molecular wave function, σ is the spin wave function and A is an operator that antisymmetrizes the wave function with respect to the three electrons. A parametric form was assumed for $F(\mathbf{x})$, the wave function of relative motion of the incident electron and the molecule,

$$F(\mathbf{x}) = (1 + a^2)^{-1/2} \{C(\xi - 1)\}^{-1} \left[\sin C(\xi - 1) + \right.$$

$$\left. + \{a + be^{-\gamma(\xi-1)}(1 - e^{-\gamma(\xi-1)})\} \cos C(\xi - 1) \right], \quad (10\text{-}50)$$

where ξ is defined in terms of the distances x_A and x_B of the incident electron from the two nuclei,

$$\xi = \left(\frac{x_A + x_B}{R} \right)$$

and

$$C = \frac{1}{2} kR.$$

The parameters a and b were determined by the Kohn variational principle and the zero order phase shift was given by

$$\eta = \left[\tan^{-1}(a) - \frac{1}{2} kR \right]. \quad (10\text{-}51)$$

The results agree quite well with the measurements of Ramsauer at energies up to 10 ev provided the exchange terms were included. This work was extended to higher order phase shifts by Carter et al. (1958).

The polarized orbital method

Temkin and Vasarada (1967) have shown that it is possible to develop the method of polarized orbitals for electron molecule scattering, so that the distortion of the molecule in the field of the electron can be allowed for, as well as exchange effects. They have discussed the case of scattering by the hydrogen molecular ion, using the single centered wave functions of Temkin (1963), discussed earlier for the target wave function.

As explained above, the internuclear axis can be considered to be fixed in space during the collision. The wave function can then be written entirely with respect to an axis fixed with respect to the internuclear line. If $\mathbf{r}_1$ and $\mathbf{r}_2$ are the position vectors of the scattered and bound electrons with respect to the center of the internuclear line as origin, then the lowest order close coupling wave function is

$$\Psi^{\pm}(\mathbf{r}_1, \mathbf{r}_2) = F(\mathbf{r}_1)\psi_g(\mathbf{r}_2, R) \pm F(\mathbf{r}_2)\psi_g(\mathbf{r}_1, R), \quad (10\text{-}52)$$

where ψ_g is the single center ground state wave function of H_2^+. The functions $F(\mathbf{r}_1)$ describing the motion of the scattered electron can be expanded in the usual way as

$$F(\mathbf{r}) = \sum_{\ell,m} r^{-1} f_{\ell,m}(r) Y_{\ell,m}(\theta,\varphi). \tag{10-53}$$

Because the H_2^+ molecule is not spherically symmetrical, the radial wave functions and the corresponding phase shifts depend on m as well as ℓ and in general the equations for different ℓ are coupled. These equations are found by requiring

$$\int \psi_g^*(\mathbf{r}_2) Y_{\ell,m}^*(\theta_1,\varphi_1)[H - E]\Psi^{\pm}(\mathbf{r}_1,\mathbf{r}_2)\, d\mathbf{r}_2 d\Omega(\theta_1,\varphi_1) = 0. \tag{10-54}$$

The unitarity of the S-matrix requires that asymptotically $f_{\ell,m}(r)$ shall be determined by real phase shifts $\delta_{\ell,m}$ and that

$$f_{\ell,m}(r) \sim \sqrt{4\pi(2\ell+1)}\, \frac{1}{k}\, i^\ell e^{i\delta_{\ell,m}} \sin\left(kr - \frac{1}{2}\ell\pi + \delta_{\ell,m}\right). \tag{10-55}$$

The transition matrix in the rotating coordinate system is then

$$\langle \ell,m| T |\ell',m'\rangle = \delta_{\ell\ell'}\delta_{mm'}\, \epsilon^{i\delta_{\ell,m}} \sin\delta_{\ell,m}. \tag{10-56}$$

The cross section that we require is defined in terms of a fixed frame of reference in which the Euler angles of the internuclear line are (α,β,γ). If **U** is the unitary operator that corresponds to the rotation that brings the fixed frame into the rotating frame, the transition operator will be transformed as

$$\mathbf{T} \to \mathbf{U}^{-1}(\alpha,\beta,\gamma)\, \mathbf{T}\, \mathbf{U}(\alpha,\beta,\gamma). \tag{10-57}$$

The matrix elements of **U** are the rotation matrices $D_{mm'}^{\ell}(\alpha,\beta,\gamma)$ defined by Edmonds (1960), and in the laboratory frame the transition matrix elements become

$$\sum_m D_{m_1 m}^{\ell*}(\alpha,\beta,\gamma)\left(e^{i\delta_{\ell,m}} \sin\delta_{\ell,m}\right) D_{m_2 m}^{\ell}(\alpha,\beta,\gamma), \tag{10-58}$$

and the scattering amplitude is

$$f(\alpha,\beta,\gamma;\theta,\varphi) = \sum_{\ell,m,m'} \frac{1}{k} \sqrt{4\pi(2\ell+1)} \; D_{0m}^{\ell\,*}(\alpha,\beta,\gamma) \times$$

$$\times \left(e^{i\delta_{\ell,m}} \sin\delta_{\ell,m}\right) D_{m'm}^{\ell}(\alpha,\beta,\gamma) Y_{\ell,m}(\theta,\varphi), \quad (10\text{-}59)$$

where (θ,φ) are the angles of scattering ($m_1 = 0$ because the initial state is a plane wave state with no component of $\mathbf{L}$ in the direction of motion). The differential cross section averaged over all orientations of the internuclear axis is

$$\bar{\sigma}(\theta,\varphi) = \frac{1}{8\pi^2} \int |f(\alpha,\beta,\gamma;\;\theta,\varphi)|^2 \, d\alpha \, d\gamma \, d(\cos\beta), \quad (10\text{-}60)$$

and the total cross section becomes

$$\sigma_{\text{total}} = \frac{4\pi}{k^2} \sum_{\ell,m} (\sin^2\delta_{\ell,m}). \quad (10\text{-}61)$$

A more complete derivation of these formulae is given in the original paper, where it is also shown how to allow for the residual Coulomb interaction that occurs for scattering by charged ions.

The lowest order approximation of $\psi_g(\mathbf{r}_2,\mathbf{R})$ is the function $r^{-1}\varphi_0^0(r,R)$ defined as the solution of equations (10-18). The distortion of the wave function of the molecular ion by the field of incident electron can be calculated by using perturbation theory in the adiabatic approximation, as in the work of Temkin on electron-atom scattering which was discussed in Chapter 5. The wave function $\psi_g(\mathbf{r},\mathbf{R})$ is replaced by $\psi_g + \psi_g^P$ where ψ_g^P is to be calculated to first order. As ψ_g^P will only be accurate for values of $r_1 > r_2$, Temkin and Vasarada retain only the dipole contribution and write

$$\psi_g^P(r_1,r_2) = \frac{-\epsilon(r_1,r_2)}{r_1^2 r_2}\varphi_0^{Pol}(r_2)\frac{1}{\sqrt{4\pi}}\cos\theta_{12}, \quad (10\text{-}62)$$

where $\epsilon(r_1,r_2)$ is the step function

$$\epsilon(r_1,r_2) = 1, \quad r_1 > r_2$$

$$= 0, \quad r_1 < r_2,$$

and θ_{12} is the angle between $\mathbf{r}_1$ and $\mathbf{r}_2$. Then φ_0^{Pol} satisfies

$$\left\{\frac{d^2}{dr^2} - \frac{2}{r^2} - \frac{2}{R} + V_0(r,R) + E_0\right\}\varphi_0^{Pol}(r) = -2r\varphi_0^{\ o}(r).$$

The polarizability of H_2^+ is in this approximation,

$$\alpha = \frac{2}{3}\int_0^\infty \varphi_0^{\ o}(r)\varphi_0^{Pol}(r)r\ dr. \qquad (10\text{-}63)$$

The coupled equations for the radial functions are again determined from equation (10-54).

No experimental data are available to test the effectiveness of the method, but it is being applied to scattering by the hydrogen molecule H_2, for which single center wave functions have been computed and it seems likely that the method will be as effective as it is for electron-atom collisions.

Numerical calculations show that in the case of electron scattering by He_2^+, both exchange and polarization effects are important. Because of the elongation of the molecule along the internuclear line, the phase shifts of the p waves turn out to be larger than those for the s waves. The asymptotic form of the potential acting on the p waves is attractive and behaves like $-r^{-3}$, so that the variation of the phase shifts with energy near the threshold will be different from the atomic case.

10-4   LONG RANGE FORCES AND ROTATIONAL EXCITATION

It is not until very low energies are reached that the energy loss through rotational excitation becomes important compared with elastic scattering. However, at low energies, the most important interaction is the long range part of the effective potential seen by the scattered electron. This is much more effective in producing rotational excitation than the short range part of the interaction, because the short range interaction will only scatter electrons in the S state at low energies, but the long range interaction can be quite effective in producing significant scattering in the states of non-zero angular momentum, and it is these states that are concerned in rotational excitation.

The effective interaction between the scattered electron and the molecule can be expressed as an optical model potential $V(\mathbf{x},\mathbf{R})$ where $\mathbf{x}$ is the position vector of the electron relative to the center of mass of the molecule and $\mathbf{R}$ is as

usual the internuclear axis. The static first order approxima-
tion to $V(\mathbf{x}, \mathbf{R})$ is

$$V_s(\mathbf{x}, \mathbf{R}) = \int d\tau |\psi_0(r_i, R)|^2 \left(\sum_i \frac{1}{|\mathbf{x} - \mathbf{r}_i|} - \frac{Z_A}{r_A} - \frac{Z_B}{r_B} \right),$$

(10-64)

where ψ_0 is the ground state electronic wave function of the
molecule and the integration is over the coordinates of the
bound electrons. The distance of the scattered electron from
each nucleus is r_A and r_B, so that for a homonuclear molecule

$$r_A = \left| \mathbf{x} + \frac{1}{2} \mathbf{R} \right|,$$

$$r_B = \left| \mathbf{x} - \frac{1}{2} \mathbf{R} \right|.$$

From (10-30) the scattering amplitude for rotational or vibra-
tional excitation is given in the Born approximation by

$$2\pi f_{fi}(\theta, \varphi) = \int d\mathbf{R} \int d\mathbf{x} \, P^*_{\nu'}(R) Q^*_{j', m'}(\theta, \Phi) e^{-i\mathbf{k}_f \cdot \mathbf{x}} \times$$

$$\times V(\mathbf{x}, \mathbf{R}) P_\nu(R) Q_{j, m}(\Theta, \Phi) e^{+i\mathbf{k}_i \cdot \mathbf{x}}.$$ (10-65)

Following earlier work of Massey (1935), Wu (1947) and Morse
(1953), Carson (1954) approximated $V(\mathbf{x}, \mathbf{R})$ by the sum of two
potentials depending on r_A and r_B respectively. For a homo-
nuclear molecule

$$V(\mathbf{x}, \mathbf{R}) \approx U(r_A) + U(r_B),$$ (10-66)

where $U(r)$ has the parametric form

$$U(r) = r^{-1}(1 + Zr) e^{-2Zr}.$$ (10-67)

The parameter $Z(R)$ is an effective nuclear charge represented
in the form

$$Z = \alpha + (R - R_0)\beta.$$ (10-68)

The parameters α and β were determined from variational
calculations to be for molecular hydrogen $\alpha = 1.166$, $\beta = -0.23$

($R_0 = 1.4$) in atomic units.

This interaction is short range in character and does not succeed in reproducing the experimental results, either for rotational or for vibrational excitation, the calculated cross section being an order of magnitude too small. To investigate the forces of longer range, $V(\mathbf{x}, \mathbf{R})$ can always be expanded in a multipole series for $x > R$. For a Σ state, the system is axially symmetrical about $\mathbf{R}$ so that,

$$V(\mathbf{x}, \mathbf{R}) = \sum_{n=0}^{\infty} \frac{U_n(R)}{x^n} P_n(\cos a), \qquad (10\text{-}69)$$

where a is the angle between $\mathbf{x}$ and $\mathbf{R}$. To see the significance of the terms in this series we can approximate $V(\mathbf{x}, \mathbf{R})$ by $V_s(\mathbf{x}, \mathbf{R})$ given by (10-64), for a homonuclear molecule. Then $V_s(\mathbf{x}, \mathbf{R})$ can be written as

$$V_s(\mathbf{x}, \mathbf{R}) = -\frac{Z}{|\mathbf{x} - 1/2\,\mathbf{R}|} + \frac{Z}{|\mathbf{x} + 1/2\,\mathbf{R}|} -$$
$$- \int d\mathbf{r}' \frac{\rho(\mathbf{r}', \mathbf{R})}{|\mathbf{x} - \mathbf{r}'|}, \qquad (10\text{-}70)$$

where $\rho(\mathbf{r}, \mathbf{R})$ is the charge density in the molecule, when the internuclear separation is R. For Σ states, ρ is axially symmetrical about $\mathbf{R}$. Expanding the denominators in (10-70), and comparing with (10-69), we see that $U_n(R) = 0$ for n odd, because $V_s(\mathbf{x}, \mathbf{R}) = V_s(-\mathbf{x}, \mathbf{R})$ for both gerade and ungerade states. For even n,

$$U_n(R) = 2Z\left(\frac{R}{2}\right)^n - \int d\mathbf{r}' \, \rho(\mathbf{r}', \mathbf{R}) r'^n P_n(\cos a'), \quad (10\text{-}71)$$

while if the molecule is uncharged $U_0(R)$ also vanishes. In discussing rotational excitation, the average of $V(\mathbf{x}, \mathbf{R})$ over the ground state vibrational function $P_0(R)$ is required and the Born approximation reduces to

$$+2\pi f_{fi} = \int d\mathbf{x} \int d\cos\Theta \int d\Phi \, e^{i\mathbf{K}\cdot\mathbf{x}} Q_{j',m'}^{*}(\Theta, \Phi) \times$$
$$\times Q_{j,m}(\Theta, \Phi) U(x, \cos a), \qquad (10\text{-}72)$$

where

$$U(x, \cos a) = \int_0^\infty P_0^2(R) V_s(x, \mathbf{R}) R^2 \, dR \tag{10-73}$$

$$\sim \sum_{n(\text{even})} \frac{C_n}{x^n} P_n(\cos a).$$

The lowest non-vanishing term in the expansion for homo-nuclear molecules is the quadrupole with $n = 2$, and Gerjuoy and Stein (1955a,b) have discussed the rotational excitation of N_2 and H_2 by retaining this term alone. The ground states of H_2 and N_2 are Σ states, and the rotational wave functions reduce to spherical harmonics $Y_{j,m}(\Theta, \Phi)$. This simplification allows the Born approximation to be evaluated analytically with the result, after summing over all m and m',

$$\sigma_{j,j'}(\Theta) = \frac{k_f}{k_i} \frac{8\pi Q^2}{45} (2j' + 1) \int_{-1}^1 d\beta \, P_{j'}(\beta) P_j(\beta) P_2(\beta), \tag{10-74}$$

where $Q \equiv C_2$ is the quadrupole moment of the molecule. The integral over the β vanishes unless $j' = j \pm 2$ and then

$$\sigma_{j,j+2} = \frac{8Q^2}{15} \pi \frac{k_f}{k_i} \frac{(j+2)(j+1)}{(2j+3)(2j+1)}$$

$$\sigma_{j,j-2} = \frac{8Q^2}{15} \pi \frac{k_f}{k_i} \frac{j(j-1)}{(2j-1)(2j+1)}. \tag{10-75}$$

The quantity that is measured experimentally is the rate at which an electron with velocity v loses energy through rotational excitation. This is

$$\frac{dW}{dt} = v \sum_j N_j \left[\sigma_{j,j+2} (E_{j+2} - E_j) - \sigma_{j,j-2} (E_j - E_{j-2}) \right], \tag{10-76}$$

where N_j is the number of molecules per unit volume and the rotational energy levels E_j are

$$E_j \approx \left(\frac{\hbar^2}{2\mu R_0^2} \right) j(j+1). \tag{10-77}$$

The energy loss per collision is

$$\left(\frac{dW}{dt} \frac{1}{nv\sigma(\text{total})} + \frac{2n}{m} W\right),$$ (10-78)

where n is the number density of the molecules and $\sigma(\text{total})$ is the total cross section. Combining (10-75), (10-76) and (10-78), the mean energy loss per collision divided by the elastic energy loss becomes

$$\lambda = 1 + \frac{32Q^2\pi}{15}\left(\frac{\hbar^2}{2\mu R_0}\right)\left(\frac{1}{W}\frac{\mu}{2m}\right).$$ (10-79)

For nitrogen, λ is ten-times the number expected from elastic loss alone and the computed value of λ, allowing for the quadrupole interaction and setting $Q = -1.1$, is the same order of magnitude as that measured which is $\lambda \sim 10$ for electron energies W between 0.1 and 0.6 ev. The quadrupole moment of hydrogen is smaller, $(Q = 0.46)$, than for nitrogen and the computed value of λ is about 2, but this is about half the measured value.[8]

The calculation of Temkin of elastic scattering of electrons by molecules showed that the distortion of the target in the field of the incident electron was most important. This will also be the case for rotational excitation. The general form of the long range interaction, modified to take polarization into account is (averaged over the vibrational ground state), for a homonuclear molecule,

$$U(x, \cos a) = -\frac{a}{2x^4} - \left(\frac{a'}{2x^4} + \frac{Q}{r^3}\right)P_2(\cos a),$$ (10-80)

where two new terms arise because the molecule can have different polarizabilities along and perpendicular to the internuclear axis, a_{11} and a_L respectively. In terms of

$$a = \frac{1}{3}(a_{11} + 2a_L),$$

$$a' = \frac{2}{3}(a_{11} - a_L).$$ (10-81)

---

[8] Crompton and Sutton (1952).

For heteronuclear molecules, the odd terms in the series
(10-69) no longer vanish by symmetry, so that the lowest
terms in the expansion of U are now

$$U(x, \cos a) \sim -\frac{a}{2x^4} - \frac{u}{x^2} P_1 (\cos a) -$$

$$-\left(\frac{a'}{2x^4} + \frac{Q}{x^3}\right) P_2 (\cos a) + \dots, \qquad (10\text{-}82)$$

where u is the permanent dipole moment of the molecule.

The importance of the polarization terms was first
pointed out by Dalgarno and Moffett (1953). For H_2 we have
that $a = 5.328$, $a' = 1.25$, while for N_2, $a = 12.0$ and
$a' = 4.2$.

The general theory of rotational excitation

To obtain an improved theory of rotational excitation,
it is necessary to go beyond the Born approximation, as well
as using a potential that allows for all the long range effects.[9]
We start from the Schrödinger equation for the system composed
of the incident electron and the target molecule:

$$\left[-\frac{\hbar^2}{2\mu} \nabla_R^2 - \frac{\hbar^2}{2m} \nabla_x^2 + \bar{H} + V(x, r_i, R) - E \right] \Psi(r_i, x, R) = 0$$

$$(10\text{-}83)$$

where $\bar{H}$ is the electronic Hamiltonian and V is the interaction
between the incident electron and the molecule. As we are
interested in transitions that leave the molecule in the lowest
electronic and vibrational levels, we introduce a projection
operator **P**, such that for large x,

$$\mathbf{P} \Psi \rightarrow \psi_0(r, R) P_0(R) \chi(x, \Theta, \Phi). \qquad (10\text{-}84)$$

A suitable form of **P** is

$$\mathbf{P} = \psi_0(r, R) P_0(R) \int_0^\infty R^2 \, dR \int dr' \psi_0^*(r', R') P_0^*(R').$$

$$(10\text{-}85)$$

---

[9] In this section we follow the work of Arthurs and Dalgarno (1960).

Introducing $\mathbf{Q} = 1 - \mathbf{P}$, we see that $\mathbf{P}\psi$ satisfies the equation

$$\mathbf{P}\left[-\frac{\hbar^2}{2m}\nabla_x^2 + H_R + U - E'\right]\mathbf{P}\psi = 0, \qquad (10\text{-}86)$$

where H_R is the Hamiltonian associated with the rotational motion of the molecule and U is the effective potential

$$U = \mathbf{P}\left[\bar{H} + V - \frac{\hbar^2}{2\mu}\nabla_R^2 - H_R + \epsilon\right]\mathbf{P} + \mathbf{P}H\mathbf{Q}\frac{1}{\mathbf{Q}(H-E)\mathbf{Q}}\mathbf{Q}H\mathbf{P}.$$
$$(10\text{-}87)$$

The energy E' is equal to $(E - \epsilon)$ where ϵ is the sum of the electronic and vibrational energies of the molecule in the ground state. The effective potential U is non-local, and contains the effects of exchange, as well as all polarization effects. To the extent that the Born-Oppenheimer separation is valid the first term in U just involves the average of the static interaction $V_s(\mathbf{x},\mathbf{R})$ given by equation (10-64) over the vibrational ground state. Equation (10-86) can be written as a wave equation for $\chi(\mathbf{x},\Theta,\Phi)$ in the form

$$\left[-\frac{\hbar^2}{2m}\nabla_x^2 + H_R + U(x, \cos a) - E'\right]\chi(\mathbf{x},\Theta,\Phi) = 0, \qquad (10\text{-}88)$$

where the long range part of U is local and is given by (10-50).

For molecules that are in a Σ state, the eigenfunctions of H_R are the spherical harmonics $Y_{j,m}(\Theta,\Phi)$ and

$$H_R Y_{j,m}(\Theta,\Phi) = E_j Y_{j,m}(\Theta,\Phi),$$
$$(10\text{-}89)$$
$$E_j = \frac{\hbar^2}{2\mu R_0^2}j(j+1).$$

The simultaneous eigenfunctions of the total angular momentum J, the angular momentum of the molecule j and of the electron ℓ are given by

$$\psi_{J,j,\ell}^M(\theta,\varphi;\;\Theta,\Phi) = \sum_{m_j}\sum_{m_\ell} C_{j\ell}(J,M;\;m_j,m_\ell)Y_{\ell,m_\ell}(\theta,\varphi) \times$$

$$\times Y_{j,m_j}(\Theta,\Phi), \qquad (10\text{-}90)$$

where M is the z component of **J**. As χ is an eigenfunction of J and M, it can be expanded as

$$\chi(\mathbf{x}, \Theta, \Phi) = \sum_{j,\ell} x^{-1} f_{j,\ell}(x) \mathfrak{y}^M_{J,j,\ell}(\theta, \varphi; \Theta, \Phi). \qquad (10\text{-}91)$$

Inserting this expression into the wave equation (10-88), it is found that the radial functions $f_{j,\ell}$ satisfy

$$\left[\frac{d^2}{dx^2} - \frac{\ell(\ell+1)}{x^2} - k_j^2 \right] f_{j,\ell}(x) =$$

$$= \sum_{j',\ell'} \frac{2m}{\hbar^2} \langle j,\ell | U | j',\ell' \rangle f_{j',\ell'}(x), \qquad (10\text{-}92)$$

where

$$k_j^2 = \frac{2m}{\hbar^2}(E' - E_j)$$

and

$$\langle j,\ell | U | j',\ell' \rangle = \int d\Omega(\theta,\varphi) \int d\Omega(\Theta,\Phi) \mathfrak{y}^{*M}_{J,j,\ell} U \mathfrak{y}^M_{J,j',\ell'}.$$

$$(10\text{-}93)$$

Having chosen a form for the effective potential U, the coupled radial equations for $f_{j,\ell}(x)$ can be solved with the usual boundary conditions, discussed in Chapter 4, to find a **K** matrix with elements $K^J_{j,\ell; j',\ell'}$. Explicit formulae for constructing the cross section from the computed **K** matrix, or **S** matrix, elements has been given by Arthurs and Dalgarno (1960).

As an alternative to solving the coupled equations exactly, the distorted wave method can be used if the coupling between the different vibrational levels is small. This is the procedure that has been followed in most applications, which differ mainly in the form assumed for U. Takayanaga and Geltman(1965) have discussed the excitation of H_2 and N_2. They represent the short range part of U as a constant and write

$$U(x, \cos a) = -\frac{a}{2L} - \left(\frac{Q}{L^3} + \frac{a'}{2L^4} \right) P_2(\cos a) x < L$$

$$\qquad (10\text{-}94)$$

$$= -\frac{a}{2x} - \left(\frac{Q}{x^3} + \frac{a'}{2x^4} \right) P_2(\cos a) x > L.$$

The cut-off parameter L was adjusted so that the elastic scattering was reproduced correctly at energies close to 10^{-3} atom units. A similar calculation by Mjolsness and Simpson (1965) differs only in that a smooth exponential cut-off is introduced to represent the short range part of U. On the other hand, Dalgarno and Henry (1965) have used the single centered wave functions of Hagstrom and Schull to calculate the potential V_S for H_2 from equation (10-64). The potential U is then found from the static interaction $V_S(\mathbf{x}, \mathbf{R})$ by averaging over the vibrational wave function

$$U \approx \int_0^\infty P_0^2(R) V_S(\mathbf{x}, \mathbf{R}) R^2 \, dR.$$

The potential U calculated in this way behaves in the correct way for small x and does not require any cut-off or modification.

Qualitatively, the effect of distortion, in the case of H_2, is to increase the cross section compared with the Born cross section, and in the case of N_2 the opposite effect is obtained. This is because of the differing sign of a in the two cases. Unfortunately the cross section is quite sensitive to the form assumed for the short range part of the interaction, so that no quantitative conclusion can be drawn. In particular it is clear that exchange will be important at low energies and this cannot be represented well by the local velocity independent forms assumed for U. The static exchange terms have been written down for scattering of electrons by hydrogen molecules by Ardill and Davison (1967). The total wave function is expressed in the form, anti-symmetric under the interchange of the three electrons 1,2,3

$$\Psi = \sum_{j,\ell} \sum_{1,2,3} r_3^{-1} f_{j,\ell}(r_3) \psi_0(r_1, r_2, R) P_0(R) \times$$

$$\times \psi_{J,j,\ell}^M(\theta_3, \varphi_3; \Theta, \Phi) \chi(1,2,3),$$

where $\chi(1,2,3)$ is a doublet spin function. The structure of the wave function is similar to that encountered in electron scattering by helium in the static exchange approximation. The coupled equations now become

$$\left[\frac{d^2}{dx^2} - \frac{\ell(\ell + 1)}{x^2} + k_j^2\right] f_{j,\ell}(x) = \frac{2m}{\hbar^2} \sum_{j',\ell'} \langle j,\ell' | U_s | j',\ell' \rangle$$

$$\times f_{j',\ell'}(x) + \sum_{j',\ell'} \int_0^\infty K_{j'\ell;\, j'\ell'}(x,x') f_{j',\ell'}(x')\, dx',$$

where the exchange kernel is defined by

$$K_{j,\ell,j,\ell'}(x,x') = (xx') \int d\Omega(\theta,\varphi) \int d\Omega(\theta',\varphi') \int d\mathbf{r} \int d\mathbf{R} \times$$

$$\times \psi_{J,j,\ell}^{M*}(\theta,\varphi;\, \Theta,\Phi) \psi_0(\mathbf{x},\mathbf{r},\mathbf{R}) P_0(R) \times$$

$$\times \frac{2m}{\hbar^2} [H - E] \psi_{J,j,\ell'}^{M}(\theta',\varphi';\, \Theta,\Phi) \psi_0(\mathbf{r},\mathbf{x}',\mathbf{R}) P_0(R).$$

These equations describe the long range quadrupole and the short range exchange effects, but the polarization terms must be added empirically to U_s.

In the case of heteronuclear molecules, scattering by the permanent dipole moment is important. If it is assumed that this is the only potential of importance, the wave equation of the incident electron becomes

$$\left[-\frac{\hbar^2}{2m} \nabla_x^2 - E - \frac{u \cos a}{x^2}\right] \psi(x) = 0. \tag{10-95}$$

Mittleman and Holdt (1965) have shown that an exact solution of this equation can be obtained, since the equation is separable in spherical polar coordinates. Here again the omitted short range effects will certainly be of importance.

Vibrational excitation

The theory of vibrational excitation can be developed along the same lines as that for rotational excitation. It is again found that the short range potential alone provides cross sections (in the Born approximation) that are of an order of magnitude smaller than those observed (Carson, 1954). To allow for the long range interactions, the Born approximation amplitude (10-65) can again be used in conjunction with the multipole expansion (10-69). The calculations of Takayanagi (1965) show that the quadrupole interaction is not capable of increasing the cross section sufficiently, but that when

allowance is made for the polarization potential (a/x^4), cross sections of the correct order of magnitude can be obtained. However in this case a cut-off at small x is introduced, so that the results are somewhat uncertain. There is no difficulty in formulating the distorted wave approximation, along the same lines as for rotational excitation and Takayanagi has shown that the influence of distortion leads to a further increase in the magnitude of the cross section.

A different approach to the same problem has been followed by Bardsley et al. (1966a,b). Using the variational method of Herzenberg they have shown that two levels of the negative hydrogen ion H_2^- exist with the configurations $(1s\sigma_g)^2 (2p\sigma_u)^2 \Sigma_u^+$ and $(1s\sigma_g)(2p\sigma_u)^2 \, {}^2\Sigma_g^+$. At energies in the region 0-12 ev, these states can be formed in an electron collision with a hydrogen molecule

$$e + H_2 \to H_2^{-\,*}.$$
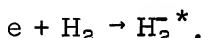
The compound state $H_2^{-\,*}$ can then decay into an electron-hydrogen molecule channel, in which the hydrogen molecule may be excited to the first or second vibrational levels

$$H_2^{-\,*} \to e + H_2\,(\nu = 0,1,2).$$
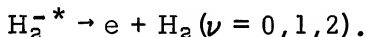
Alternatively, as the potential energy curves of the H_2 levels are repulsive, the negative molecular ion can decay into a hydrogen atom and a negative hydrogen ion

$$H_2^{-\,*} \to H + H^-. \tag{10-96}$$

The calculation of the cross section for vibrational excitation or of dissociative attachment $(e + H_2 \to H + H^-)$ follow the general principles of the Herzenberg-Mandl method outlined in Chapter 7. The existence of the H_2^- states gives rise to a broad peak from 2 to 6 ev in the excitation cross section. This is shown in Fig. 10-8 and is in harmony with the measurements of Schultz (1964), Englehart and Phelps (1963) and Ramien (1935). The cross section for dissociative attachment is shown in Fig. 10-9 and again good agreement is obtained with the experimental work of Rapp et al. (1965).

The cross sections obtained in this way are similar to those found by Takayanagi using the distorted wave method. The reason for this is that the H_2 resonance is a shape

resonance and is not a virtual bound state, associated with the opening of a new threshold, and the distorted wave potential can be of the correct shape and depth to support such a resonance.

Compound negative ion states have also been used by Chen (1965) to investigate vibrational excitation of N_2, and also by Herzenberg (1967), and Chen and Peacher (1968), in calculating the rate of associative detachment, which is the inverse reaction to (10-89)

$$H + H^- \rightarrow H_2^* + e.$$
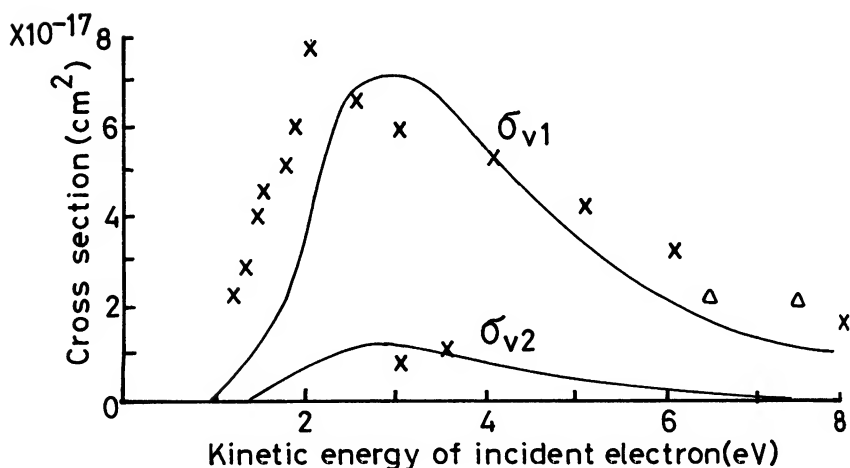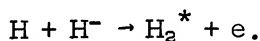
Figure 10-8.   Cross sections for excitation of the two lowest vibrational states of hydrogen, showing the influence of the $^2\Sigma_u$ metastable state of H_2^-.

──────   Calculated cross section (Bardsley et al., 1966).

+ + +   Experimental cross section (Schulz, 1944).
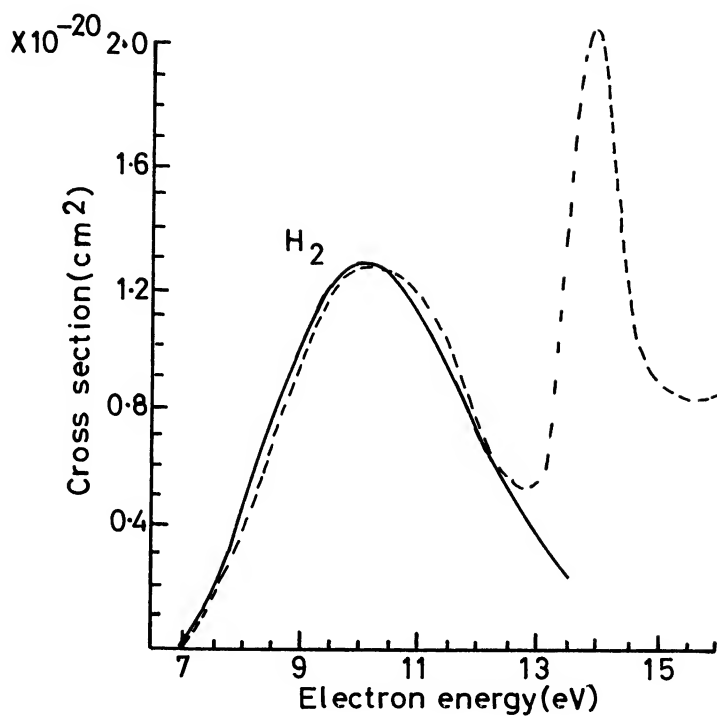
Figure 10-9. Cross section for the dissociation of the hydrogen by electron impact via the formation of the $^2\Sigma^+$ resonance in H_2^-.

—————— Calculated cross section (Bardsley et al., 1966).

- - - - - Experimental cross section (Rapp et al., 1965).

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TABLE OF ATOMIC CONSTANTS

Electron charge
$$e = 4.8029 \text{ e.s.u.}$$
$$= 1.602 \times 10^{-9} \text{ coulombs}$$

Electron mass
$$m = 9.109 \times 10^{-28} \text{ gm}$$

Proton mass
$$m = 1.66 \times 10^{-24} \text{ gm}$$

Velocity of light
$$c = 2.9979 \times 10^{10} \text{ cm/sec} = 137 \text{ atomic units}$$

Planck's constant
$$h = 6.6254 \times 10^{-27} \text{ erg-sec}$$

Bohr radius of the hydrogen atom
$$a_0 = 0.5292 \times 10^{-8} \text{ cm}$$

Ionization energy of atomic hydrogen
$$I_0 = 13.55 \text{ ev}$$

Ground state energy of hydrogen (infinite mass nucleus)
$$R_0 = 13.605 \text{ ev} = \tfrac{1}{2}(\text{atomic unit of energy}) = 1 \text{ Rydberg}$$

Electron volts
$$1 \text{ ev} = 1.601 \times 10^{-12} \text{ ergs}.$$

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